HEXABENZOCORONESES AS POTENTIAL PRECURSORS TO AROMATIC BELTS

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Hexabenzocoronenes as Potential Precursors to Aromatic Belts

by

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I dedicate this thesis with love and countless thanks to

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I declare that I am greatly indebted to those people who helped me see my dreams become true and I will always live my life having them in my heart.

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List of Symbols, Abbreviation, and Acronyms

aq.	Aqueous
Ac	acetic
Bn	benzyl
b.p.	boiling Point
Bu	butyl
CPPAs	cyclic paraphenyleneacetylenes
DDQ	1,8-Diazabicyclo[5.4.0]undec-7-ene
DIBAL	diisobutyl aluminum hydride
DMB	dimethyloxybenzyl
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
Et	ethyl
FVT	flash vacuum thermolysis
GPa	gagaPascal
HBC	hexabenzocoronene(s)
H_f	heat of formation
IEDDA	inverse electron demand Diels-Alder
IR	infrared (spectroscopy)
kcal	kilocalorie(s)
Lit	literature
Me	methyl
mol	mole(s)
MOM	mothoxymethyl
Mp	melting point

NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance (spectroscopy)
PMB	*para*-methoxymethylbenzyl
PAH	polycyclic aromatic hydrocarbons(s)
Ph	phenyl
POAV	π-orbital axis vector
PTC	phase transfer catalysis
SWCNT	single-walled carbon nanotube(s)
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
TPa	terra Pascal
Tr	trityl
UV-Vis	ultraviolet-visible (spectroscopy)
VID	valence isomerisation/dehydrogenation

Chapter 1

Polycyclic Aromatic Hydrocarbons

1.1 - Introduction

The work described in this thesis is part of a larger effort aimed at the synthesis of aromatic belts. The presentation and discussion of the results of this work (Chapter 2) will be prefaced by a review of carbon allotropes, especially the fullerenes, where the equators of which can be viewed as aromatic belts, or even as carbon nanotubes, which the targeted belts are lower homologs of. This will be followed by an introduction to the key chemistry that underpins this work: general cyclophane chemistry and the synthesis of [*n*](2,7)pyrenophanes using the valence isomerisation / dehydrogenation (VID) reaction, and the synthesis of hexabenzocoronenes via the Scholl reaction.

1.2 - Carbon and its allotropes

Coined by the Swedish chemist Jöns Jacob Berzelius (1779-1848),[1] the term "allotrope" is derived from the Greek word, *allotropia*, meaning variety of demeanor (*allos* = variety, *tropos* = habit). Applied to elements, it refers to the variance of the structural forms of an element that is characterized by the three dimensional arrangement of the atoms and the nature of the bonding between them. Each allotrope of an element has a unique set of physical and chemical properties. Elements that have allotropes include carbon, oxygen, sulfur and phosphorous. Among all elements, carbon is the element with the greatest number of allotropes discovered so far. The properties exhibited by these allotropes are not only fundamentally interesting from an academic perspective, but also the root to their commercial value.

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[1] Addison, W. E.; *The Allotropy of the Elements*, Oldourne Press, London, **1964**.

The most abundant allotrope of carbon is graphite, which was named by the German geologist Abraham Gottlob Werner[2] (1750-1817). The name comes from the Greek verb *graphein* (to draw/write) because graphite was used in the manufacturing of pencils. Graphite has a layered structure consisting of parallel sheets of sp^2-hybridized carbon atoms arranged in a hexagonal grid. Of the covalent network solids, only graphite conducts electricity. This is due to the extended π system.

Diamond is the second most abundant allotrope of carbon. It has a three-dimensional network structure in which each carbon is singly-bonded to four others with sp^3 hybridization. It is prized as a gemstone and its hardness and heat conductivity make it valuable for a variety of industrial applications such as rock grinding and drilling.

Graphite and diamond were the only known allotropes of carbon until the milestone discovery of Buckminsterfullerene in the mid 1980s.[3] This was followed by the isolation and the characterization of other form of fullerenes,[4] carbon nanotubes[5] and other allotropic nanophases of carbon.[6] (Figure 1.1)

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[2] http://en.wikipedia.org/wiki/Graphite. Accessed on 19-04-2006.
[3] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162-163
[4] a) Taylor, R.; Hare, J.; Abdul-sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423-1425. b) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843-892. c) Liu, S. Y.; Sun, S. Q. *J. Organometallic Chem.* **2000**, *599*, 74-86. d) Slania, Z.; Zhao, X.; Uhlik, F.; Lee, S.-L. *J. Mol. Struct. (Theochem)* **2003**, *630*, 205-213. e) Yang, S. F.; Dunsch, L.; *Chem. Eur. J.* **2005**, *12*, 413-419.
[5] a) Iijima, S. *Nature* **1991**, *354*, 56-58. b) Moreno, J. M. C.; Awamy, S. S.; Fujino, T.; Masahiro, Y. *Chem. Phys. Lett.* **2000**, *329*, 317-322.
[6] Qin, L. C.; Iijima, S. *Chem. Phys. Lett.* **1996**, *262*, 252-258.

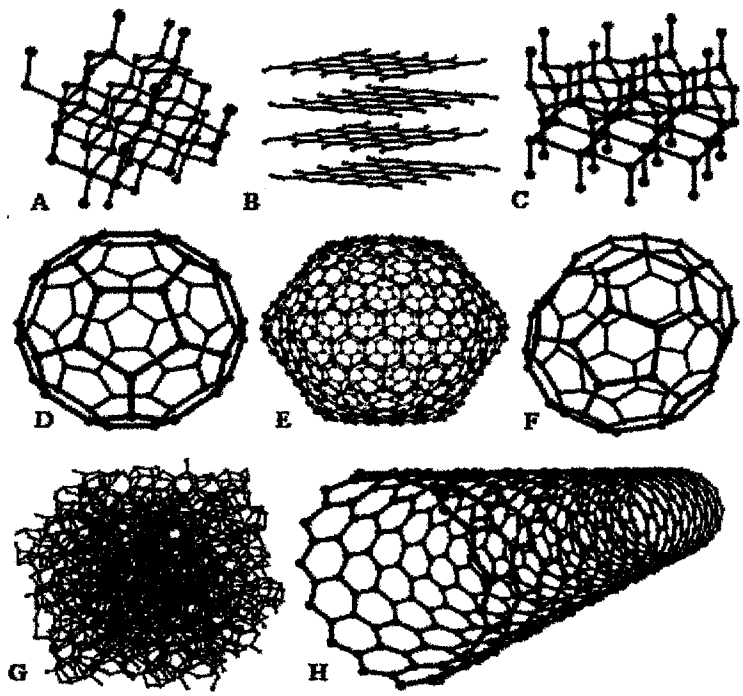


Figure 1.1: Examples of carbon allotropes: A) diamond, B) graphite, C) londsdaleite (hexagonal diamond), D) C_{60}, E) C_{540} (a hypothetical allotrope), F) C_{70}, G) amorphous carbon, H) a single-walled carbon nanotube.

Beyond the known allotropes of carbon, there is an infinite number of hypothetical allotropes. These can be "constructed" from various combinations of the three stable hybridization states of carbon: sp^3, sp^2, and *sp*. One way of generating hypothetical carbon allotropes is to "insert" units of sp-hybridized carbon consisting of an even number of atoms into the various C-C bonds of other carbon allotropes.[7] This strategy can be applied to closed and open structures alike. For example, insertion of thirty C_4 units of *sp*-hybridized carbon into C_{60} affords the "expanded" fullerene C_{180} (Figure 1.2, A and B). Graphene (a single sheet of graphite) can be expanded in a similar fashion by the insertion of sp-hybridized C_2 units to give

[7] Chauvin, R. *Tetrahedron Lett.* **1995**, *36*, 397-400.

"graphyne"[8] (Figure 1.2, C). Expanded diamond (Figure 1.3, D) is arrived at by an analogous process.

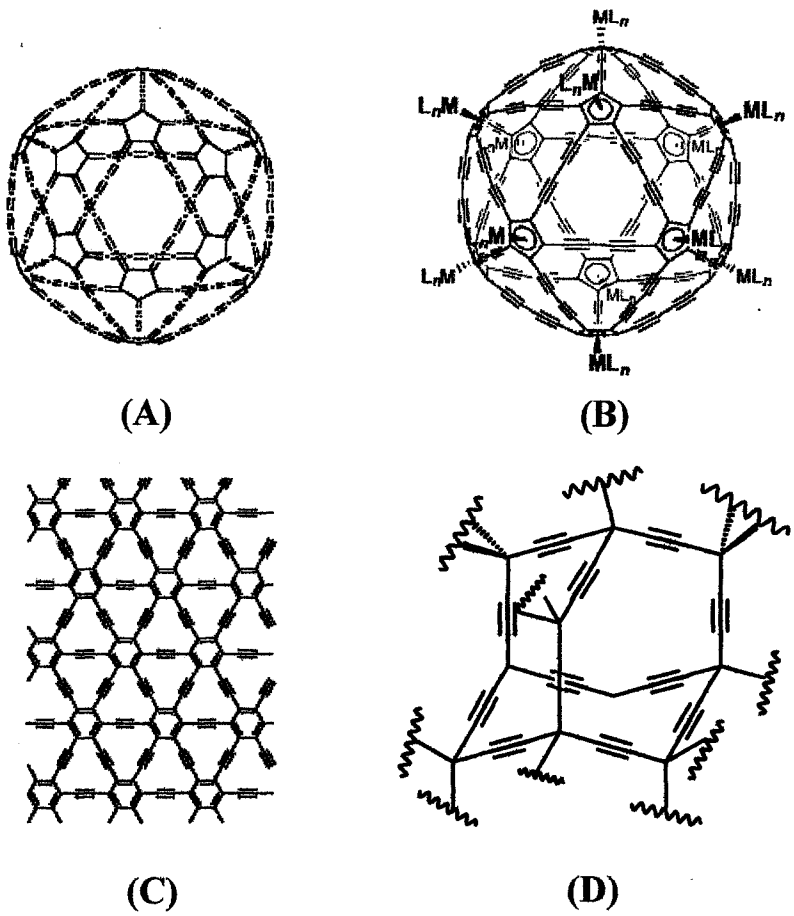


Figure 1.2: Examples of hypothetical carbon allotropes containing sp-hybridized carbon atoms. A) C_{180} (stabilized by complexation), B) C_{180}, C) graphyne, D) expanded diamond.

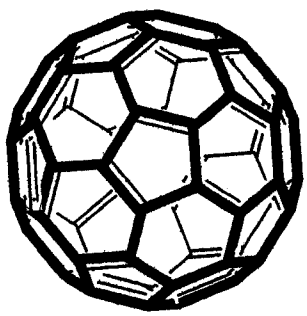
1.3 - Buckminsterfullerenes

In 1985, Robert F. Curl, Sir Harold W. Kroto and Richard E. Smalley were conducting experiments at Rice University aimed at understanding the mechanisms by which long chained carbon molecules are formed in interstellar space and

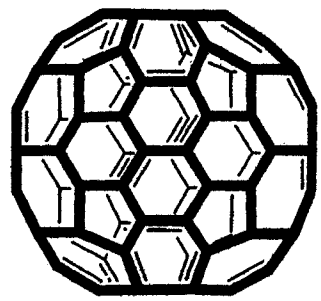
[8] a) Haley, M. M.; Brand, S. C.; Pak, J. J. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 836-838. b) Wan, W. B.; Brand, S. C.; Pak, J. J; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 2044-2052. c) Vögtle, F.; Stoddart, J. F.; Shibasaki, M.; *Stimulating Concepts in Chemistry*, Wiley-VCH, Weinheim, **2000**. d) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107-119.

circumstellar shells. Graphite was vaporized by laser irradiation, producing a remarkably stable cluster, which was composed of exactly 60 carbon atoms.[3]

This cluster was soon shown to consist of only sp^2-hybridized carbon atoms arranged into a truncated icosahedron, *i.e.* a polygon comprised of twelve five-membered rings and twenty six-membered rings. The name "Buckminsterfullerene" was given to this new carbon allotrope in recognition of the American architect and engineer R. Buckminster Fuller[9] (1895-1985), who built geodesic structures based on Euler's theorem.[10] Although it is often used to refer specifically to C_{60}, the term "fullerene" is a generic term that encompasses all closed allotropes of carbon consisting of twelve five-membered rings and any number of six-membered rings. The inclusion of a point group and the number of carbon atoms in the name allows for the designation of a specific fullerene. Buckminister fullerene is, formally, I_h-C_{60}-fullerene and **(2)** is D_{5h}-C_{70}-fullerene.



(1)



(2)

In 1990, Krätschmer and co-workers reported a method for the preparation and isolation of C_{60} in macroscopic quantities.[11] They found that using resistive heating in a helium atmosphere to vaporize graphite produced a grimy condensate, from which

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[9] Billups, W. E.; Ciufolini, M. A.; *Buckminsterfullerenes*, VCH, New York, **1993**.
[10] http://www.neubert.net/Geodesic/Pict/GEODesic.html. " Accessed on 04-20-2006"
[11] Krätschmer, W.; Lamb. L. D.; Fostiropoulos, K. *Nature* **1990**, *347*, 354-358.

fullerenes C_{60} **(1)** and C_{70} **(2)** were separated by chromatography. C_{60} **(1)** is still the most abundant fullerene and C_{70} **(2)** the second most abundant fullerene. The smallest possible form of fullerene is C_{20} which is a structure that is built solely by five membered rings.[12]

With access to multigram quantities of C_{60} and (and also C_{70}), attention was directed toward investigating their chemical and physical properties[13] (*e.g.* aromatcity) and their chemical behavior.[14] There is no upper limit to the size of a fullerene, but the largest fullerene to be isolated and characterized is a didysprosium containing fullerene of C_{100} and the second largest isolated and characterized fullerene is a tridysprosium fullerene of C_{98}.[15] The understanding of fullerene chemistry naturally led to the successful synthesis of multiply functionalized forms of fullerenes[16] and the use of fullerenes as components of dendrimers and polymers.[17]

1.4 - Carbon nanotubes

1.4.1 - Overview

Known also as "buckytubes", carbon nanotubes are tubular nano-constructed carbon molecules consisting of graphitic sheets wrapped around a central axis in the form of a tube.[18] Like graphite, they are composed entirely of sp^2 hybridized carbon atoms that map onto a hexagonal grid and they exhibit exceptional tensile strength and thermal conductance.[19] Their chemical and electronic properties[17] (*e.g.* molecular

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[12] Prinzbach, H.; Weller, A.; Landenberger, P.; Wahl, F.; Wörth J.; Scott, L. T.; Gelmont, M.; Olevano, D.; Issendorff, B. V. *Nature* **2000**, *407*, 60-63.
[13] Sternfeld, T.; Thilgen, C.; Hoffman, R. E.; Heras, M. R. C.; Diederich, F.; Wudl, F.; Scott, L. T.; Mack, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **2002**, *124*, 5734-5738.
[14] Hirsch, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1138-1141.
[15] Yang, S.; Dunsch, L. *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 1299-1302.
[16] Sergeyev, S.; Schär, M.; Seiler, P.; Lukoyanova, O.; Echegoyen, L.; Diederich, F. *Chem. Eur. J.* **2005**, 1-11.
[17] a) Taylor, R.; Walton, M. *Nature* **1993**, *363*, 685-693. b) Wang C.; Guo, Z-X.; Fu, S.; Wu, W.; Zhu *Prog. Polym. Sci.* **2004**, *29*, 1079-1141.
[18] a) McEuen, P. L.; Fuher, M.; Park, H. *Nanotech.* **2002**, *1*, 78-85. b) Heer, W. A.; Bonard, J-M.; Fauth K.; Châtelain, A.; Forró, L.; Ugarte, D. *Adv. Matter.* **1997**, *9*, 87-89.
[19] Berber, S.; Kwon, Y. K.; Tománek, D. *Phys. Rev. Lett.*. **2000**, *84*, 4613-4616.

wires, optical conductivity and d.c. transport) make them potentially useful materials in wide variety of applications and modern technology.

1.4.2 - Discovery

Working with an experimental set-up similar to those used for the production of C_{60}, Iijima reported in 1991 the discovery of macromolecular analogs of fullerenes.[5] These tubular structures, which are now known as carbon nanotubes, were produced in an arc-discharge apparatus in which a large current was drawn as a spark between two carbon electrodes. Based on high–resolution transmission electron microscope imaging, it was concluded that the structures were a hitherto unknown form of elemental carbon, in which a number of concentric shells of rolled up graphite sheets formed long needles with a helical fine structure. These tubes, which are now referred to as "multi-walled carbon nanotubes", were only a few nanometers in diameter, but many micrometers long. Interestingly, similar structures of filments formed at graphitic arc temperatures consisting of cylindrical layers or "scroll-like formations" had been observed in the 1960s by Bacon.[20] However, these were interpreted as rolled-up "spiral cross sections" of a single sheet of graphite, graphene, not as tubes. Against the backdrop of the discovery of the fullerenes, Iijima's discovery received far more attention than Bacon's scrolls ever did.

A few months after the report of the discovery of multi-walled carbon nanotubes, the first theoretical papers on individual tubes, or "single-walled carbon nanotubes" (SWCNTs) appeared.[21] Scientists predicted interesting properties of single tubes made from graphene due to their essentially one-dimensional structure. Thus, when these single-walled carbon nanotubes were discovered in 1993,[22] the field of

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[20] Bacon, R. *J. App. Phys.* **1960**, *31*, 283-290.
[21] a) Mintmire, J. W.; Dunlap, B. I.; White C. T. *Phys Rev. Lett.* **1992**, *68*, 631-634. b) Hamada, N.; Sawada, S. I.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579-1581.
[22] Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603-605.

nanotube research quickly took off. However, as the material grown with the early techniques consisted of only a few percent of nanotube material (the rest was soot, fullerenes and other impurities), theory remained well ahead of experiments until large scale production methods were developed, *e.g.* arc discharge,[23] thermal deposition of hydrocarbons,[24] and catalyzed chemical vapor deposition.[25]

1.4.3 - Structural and physical properties.

Even though it is not the way in which nanotubes are formed, the most intuitive way to illustrate the structure of nanotubes involves rolling up a single sheet of graphite, *i.e.* graphene. This is illustrated in (Figure 1.3).[26]

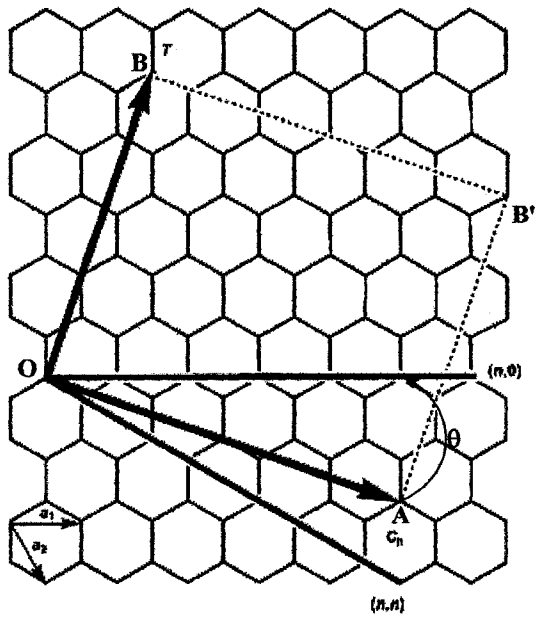

Figure 1.3: Schematic representation of a 2D graphite layer with the lattice vectors.

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[23] a) Ebbsesen, T. W.; Ajayan, P. M.; *Nature* **1992**, *358*, 220-222. b) Colbert, D. T.; Zhang, J.; McClure, S. M.; Nikolaev, P.; Chen, Z.; Hanfer, J. H.; Owens, D. W.; Kotula, P. G.; Carter, C. B.; Weaver, J. H.; Rinzler, A. G.; Smalley, R. E. *Science* **1994**, *266*, 1218-1222. c) Bethune, D. S.; Klang, C. H.; De Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605-607.

[24] a) Ivanov, V.; Nagy, J. B.; Lambin, P.; Lucas, A.; Zhang, X. B.; Zhang, X. F.; Bernaerts, D.; Tendeloo, G. V.; Amelinckx, S.; Landuyt, J. V. *Chem. Phys. Lett.* **1994**, *223*, 329-335.

[25] Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zou, B. S.; Zhou, W. Y.; Zhao, R. A.; Wang, G.; *Science* **1996**, *274*, 1701-1703.

[26] a) Hirsch, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1853-1859.

The vector OA connects two equivalent points of graphene and OB is a vector of arbitrary length perpendicular to OA. The point B` completes a rectangle with points O, A and B (or a square when OA is the same length of as OB). The graphene sheet can then be "cut" along the parallel vectors OB and AB` and then the resulting strip of graphene rolled into a tube by fusing vectors OB and AB` such that points B and B` intersect and points O and A intersect. The unit cell of the tube is then specified by OA, which is called the chiral vector C_h, and the lattice vector T, which is defined by the first intersection along OB with the point of graphene lattice. The chiral vector itself can be expressed in terms of the unit vectors a_1 and a_2, which are the primitive lattice vectors of the hexagonal lattice.[27] In this way, a particular nanotube is most often specified by pair of integers (n,m) such that $C_h = na_1 + ma_2$. The various parameters are related mathematically such that, for instance, the diameter of the nanotube can be calculated from just the indices (n,m). Nanotubes are typically divided into three groups based on the visual appearance of their physical structure: armchair nanotubes (*e.g.* A in Figure 1.4) where $C_h = (n,n)$, zigzag nanotubes (*e.g.* B in Figure 1.4) where $C_h = (n,0)$ and chiral nanotubes where $C_h = (n,m)$ (*e.g.* C in Figure 1.4)

[27] Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787-1799.

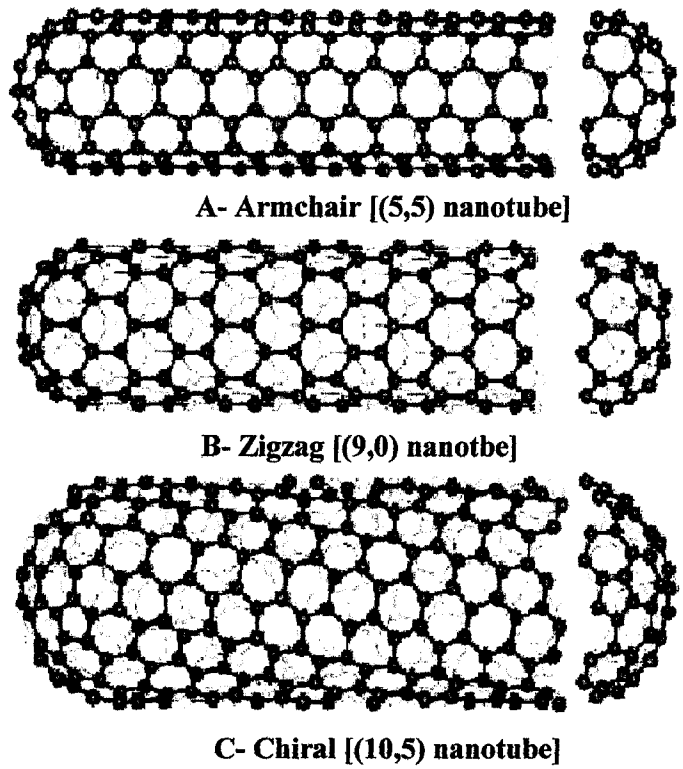

Figure 1.4: Idealized representation of defect-free (*n*,*m*) SWCNTs with one open end.

The examples shown in Figure 1.4 each have one "closed" end (to the left), where a hemifullerene (containing exactly six five-membered rings) "caps" the nanotubes, and one "open" end (to the right). The cap required to close the right hand end is also shown. The nanotube and its cap must obviously have the same topology about their rims, and it was in fact the visual appearance of the topologies that led to the names "armchair" and "zigzag". The term "chiral" derives from the fact that such systems and indeed chiral.

Carbon nanotubes possess distinctive mechanical and electronic properties, which depend upon their geometry and dimensions. They were found to have very high Young's moduli (about 1 TPa) and tensile strength approaching 60 GPa.[28] They

[28] a) Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678-680. b) Wong, E. W.; Sheehan, P.; Lieber, C. M. *Nature* **1997**, *277*, 1971-1975.

exhibit superb mechanical properties[29] and their electronic properties depend upon their diameter and helicity, which is determined by the roll-up vector.[30] According to Ajayan and others[26,27,31] all armchair nanotubes are conductors. The same is true for those chiral and zigzag nanotubes where the ratio $(n-m)/3$ is a whole number. All other nanotubes are semiconductors. Much has been made of the potential of carbon nanotubes,[32] but it is safe to say that very little of this potential has yet been realized. However, much work is being done in this area. The unique electronic properties of carbon nanotubes render them potential components of electronic devices such as field effect transistors,[33] electronic field emitters[34] and other future generation electronic devices.[35] Their exceptional stiffness and strength along their length has already been used to tremendously enhance the mechanical strength of silicon dioxide ceramics.[36]

Single-walled carbon nanotubes are polydisperse macromolecules. Every sample of nanotubes that has ever been generated consists of tubes of varying length, diameter and helicity. Although individual tubes have been successfully imaged,[37] the resolution has never been high enough to identify the indeces (n,m). Being polydisperse systems, carbon nanotubes are generally characterized by parameters such as average molecular weight, average diameter and average length. Considerable effort is being invested in ways of improving the production techniques and ways in narrowing the degree of polydispersity.

---

[29] Dalton, A. B.; Collins, S.; Muñoz, E.; Razal, J. M.; Eborn, V. H.; Ferraris, J. P.; Coleman, J. N.; Kim B G.; Baughman, R. H. *Nature* **2003**, *423*, 703.
[30] Ormsby, J. L.; King, B. J. *J. Org. Chem.* **2004**, *69*, 4287-4291
[31] a) Xie, S. S., Chang, B. H.; Li, W. Z.; Pan, Z. W.; Sun, L. F.; Mao, J. M.; Chen, X. H.; Qian, L. X.; Zhou, W. Y. *Adv. Mater.* **1999**, *11*, 1135-1138. b) Dai, L.; Mau, W. H. *Adv. Mater.* **2001**, *131*, 899-913.
[32] Peterson, C. *Computer* **2000**, *33*, 46-53.
[33] Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. *Appl. Phys. Lett.* **1998**, *73*, 2447-2449.
[34] Baughman, R. H.; Zakhidov, A. A.; Heer, W. A. D. *Science* **2002**, *297*, 787-792
[35] Saito, S. *Science* **1997**, *278*, 77-78,
[36] Hwang, G. L.; Hwang, K. C. *J. Mater. Chem.* **2001**, *11*, 1722-1725.
[37] Odom, T. W.; Huang, J-L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62-64

The use of nanotubes for materials applications or molecular electronics has been slow in coming due to their insolubility or near insolubility in most organic solvents and their propensity to form "bundles" held together by Van der Waal's forces. These problems rule out processing using existing methods. Consequently, approaches such as sidewall functionalization[38] are being investigated to circumvent these problems. Again, the polydispersity of the nanotubes means that a precise picture of what is occurring at the molecular level is not obtainable. "Synthesis", which applies to monodisperse systems, is not yet a term that can be applied to SWCNTs.

The first method from which carbon nanotubes were produced in bulk quantities is arc-discharge. The plasma in the spark between the electrodes evaporates the carbon material, which then "condenses" as carbon nanotubes. The carbon addition of a small percentage of a catalyst in the carbon electrode can facilitate the production of single-walled carbon nanotubes.[39] Other methods such as laser ablation[40] and chemical vapor deposition[41] were used later on. Despite the fact that these techniques are by far the most widely used, some other fascinating new methods have also been developed as well, such as growth from wafers of silicon carbide annealed in vacuum[42] or mesoporous silica thin film used in carbon vapor deposition experiments.[43] Some work aimed at controlling the width of nanotubes using chemical vapor deposition has also been done.[40]

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[38] Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem. Int. Ed.* **2001**, *40*, 4002-4005.
[39] Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Chapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756-758.
[40] Zhang, Y.; Iijima, S. *Appl. Phys. Lett.* **1999**, *75*, 3087-3089.
[41] Cheung C. L.; Kurtz, A.; Park, H.; Lieber, C. M. *J. Phys. Chem. B.* **2002**, *106*, 2429-2433.
[42] Derycke, V.; Radosavljević, M.; Ross, F. M.; Avouris, Ph. *Nano Lett.* **2002**, *2*, 1043-1046.
[43] Murakami, Y.; Yamakita, S.; Okubo, T.; Maruyama, S. *Chem. Phys. Lett.* **2003**, *375*, 393-398.

1.5 - Large polycyclic aromatic hydrocarbons

1.5.1 - Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been subjects of intense research work for a long time. As discussed below, there is a great structural diversity in this class of compounds. Stability, however, can range from very high to very low depending upon the structure. In this regard, issues such as aromaticity and electronic structure have been especially important topics for theoretical studies. PAHs have not only stood as challenging synthetic targets, but have also been used as starting materials, building blocks and scaffolds for more elaborate systems. Many PAHs are biologically active, with carcinogenicity being a common characteristic.

PAHs can be constructed conceptually by the multiple fusion of benzene units. There are numerous fusion motifs available and these give rise to several distinct families of PAHs, for example, successive fusion of benzene units in a linear fashion (Figure 1.5) gives the "linear acenes" or "[*n*]acenes". Similarly, the [*n*]phenacenes are constructed by iterative angular fusion (Figure 1.6).

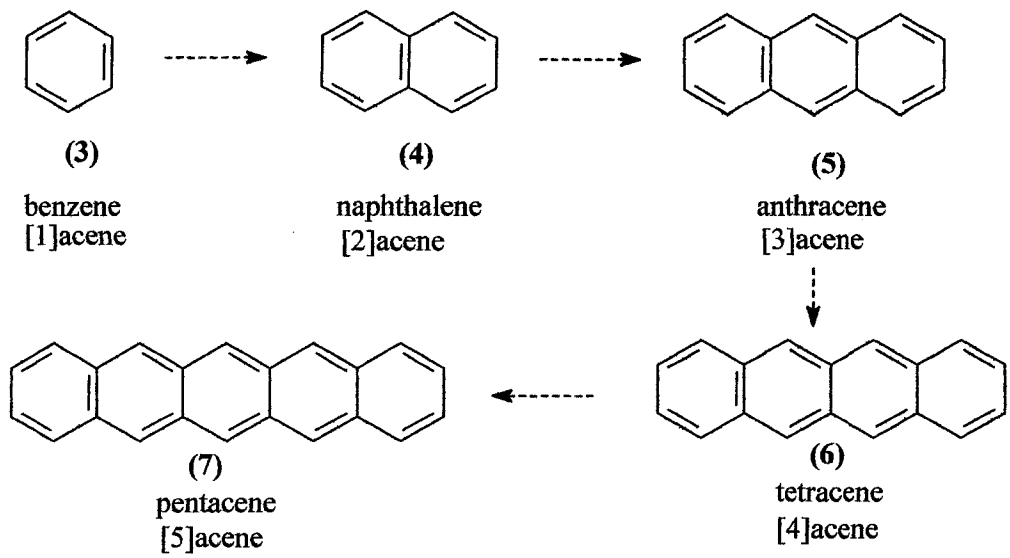


Figure 1.5: The [*n*]acenes.

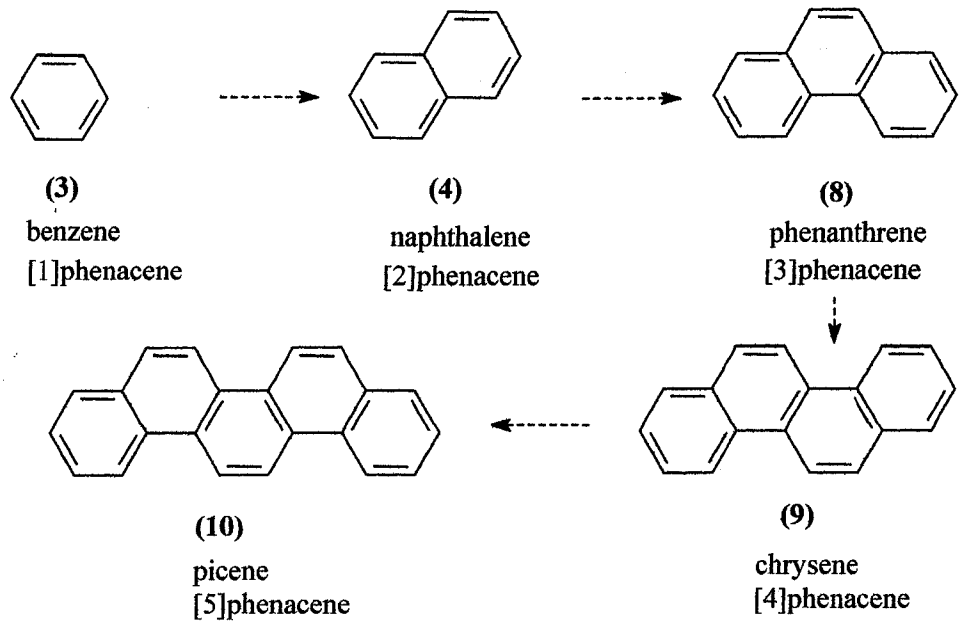


Figure 1.6: The [*n*]phenacenes.

Another class of PAHs is constructed from the complete fusion of benzene units to the circumference of a parent system (circumfusion). For example, circumfusion of cyclopentadiene (radical) gives corannulene **(12)** (circumcyclopentadiene) and circumfusion of benzene affords coronene **(13)** (circumbenzene) (Figure 1.7). Circumfusion of coronene gives circumcoronene **(14)** and repeated circumfusion rapidly approaches graphene. Up until recently, the synthesis of large segments of graphene was thwarted by solubility problems and the lack of suitable synthetic methodology.

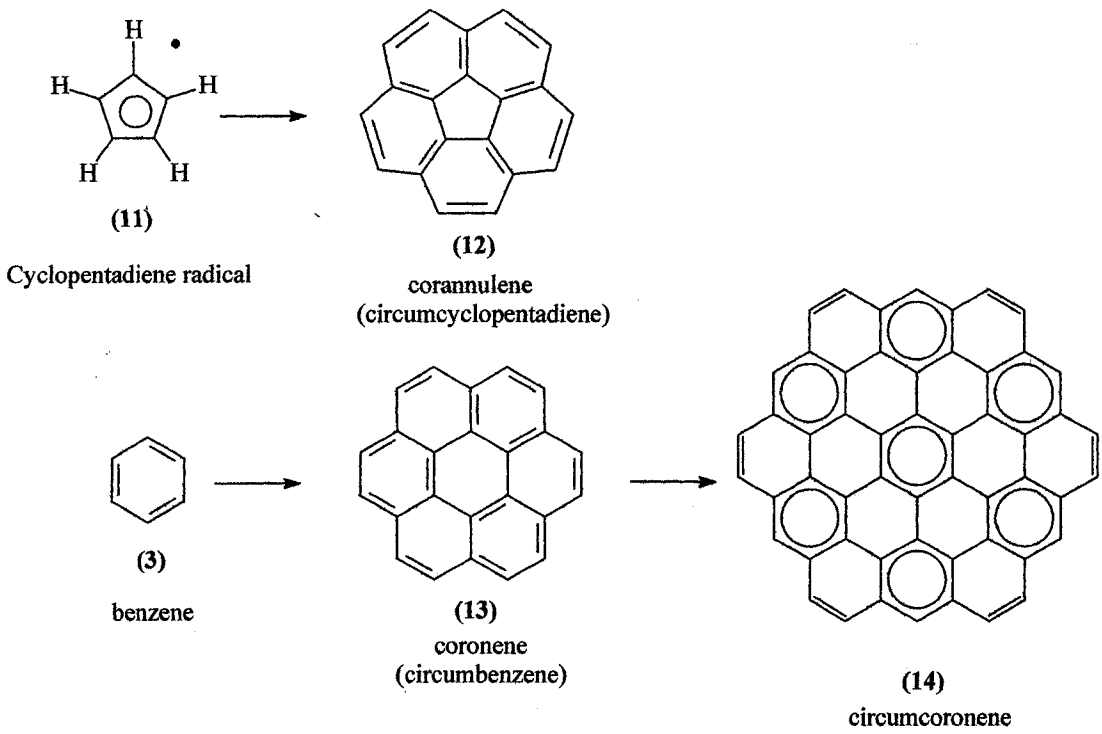
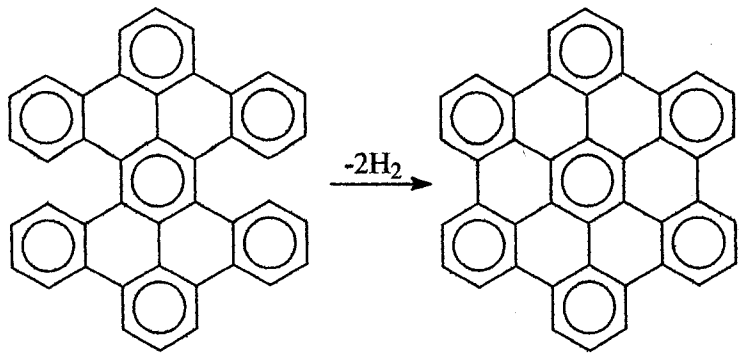


Figure 1.7: Circumfusion of cyclopentadienyl radical and benzene.

1.5.2. - Hexabenzocoronenes

Hexabenzocoronene **(15)** is a C_{42} PAH with D_{6h} symmetry. It was first reported in 1958 by Clar as a pale yellow crystalline hydrocarbon with stability so great that the determination of its melting point was not attainable.[44] Clar's synthesis of HBC was based on melting tetrabenzoperopyrene **(16)** at 482 °C with the evolution of hydrogen and the formation of **(15)** (Scheme 1.1).

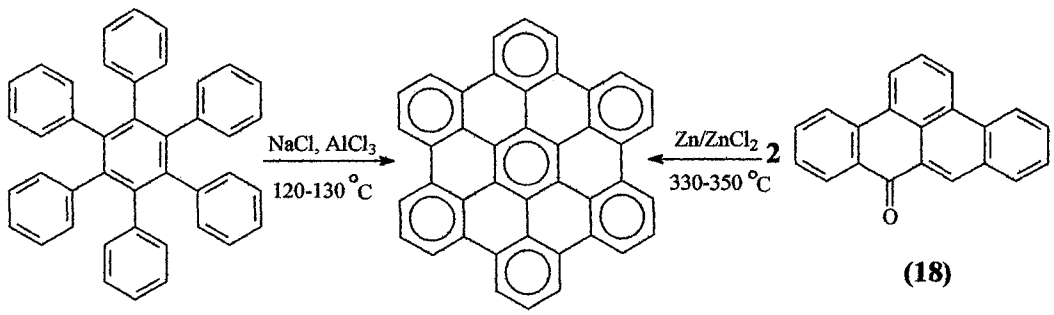
[44] a) Clar, E.; Ironside, T.; Zander, M. *J. Chem. Soc.* **1959**, 142-147. b) Clar, E.; *Polycyclic Hydrocarbons I-II*, Academic Press, London **1964**. c) Harvey, R. G.; *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, New York, **1997**.



(16) **(15)**

Scheme 1.1: Clar's synthesis of HBC **(15)**.

Halleux and colleagues also reported the synthesis of the same compound from a NaCl-$AlCl_3$ melt of hexaphenylbenzene (Scheme 1.2).[45] In the same paper, these authors also reported that dibenzanthrone **(18)** could be converted into **(15)** upon treatment with Zn/$ZnCl_2$. In the mid 1980s, a newer synthesis of **(15)** was reported by Schmidt and colleagues who provided detailed spectral data (UV, IR, fluorescence, photoelectron and phosphorescence)[46] about compound **(15)**.

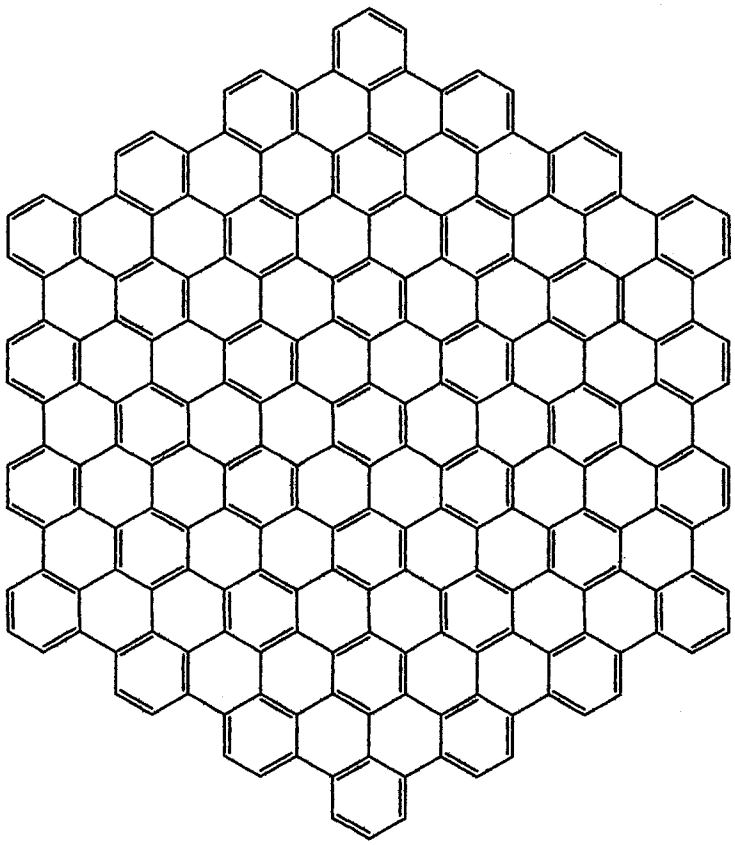


(17) **(15)** **(18)**

Scheme 1.2: Halleux's synthesis of HBC **(15)**

[45] Halleux, A.; Martin, R. H.; King, G. S. D. *Helv. Chim. Acta* **1958**, *78*, 4765-4770.
[46] Hendel , W.; Khan, Z. H.; Schmidt, W. *Tetrahedron* **1986**, *42*, 1127- 1134.

It was not until the mid 1990's that Müllen reported a new and much improved synthetic methodology[47] (see Section 1.5.4), which enables the rapid synthesis of gram quantities of HBCs. This methodology has since been used to synthesize a wide range of HBCs and related systems. Some very large PAHs have been synthesized, which can be viewed as molecular graphene segments. The largest one yet reported[48] is the C_{222} system **(19)** (Figure 1.8).



(19)

Figure 1.8: $C_{222}H_{42}$ reported by Müllen.

[47] Stabel, A.; Herwig, P., Müllen, K., Rabe, J. P. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 16009-1611.
[48] a) Iyer, V. S.; Wehmeier, M.; Brand, D.; Keegstra, M.; Müllen K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1604-1607. b) Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Pryzbilla, L.; Räder, H. J.; Müllen, K. *Chem. Eur. J.* **2002**, *8*, 1424-1429.

1.5.3 - Structure and properties

The shape of hexabenzocoronene naturally invites comparison with benzene. Like benzene, HBC is a sixfold symmetric system with a coplanar arrangement of all of its atoms in its lowest energy conformation. According to Clar, this compound belongs to the most stable group of aromatic hydrocarbons known as "fully benzenoids" whose ground states are best described by the structural formula **(15)**, which is composed of seven (resonant) sextets and six "empty" rings.[49] Robertson and Trotter reported the first crystal structure of HBC using diffraction data collected from a twinned crystal.[50] The bond lengths were consistent with Clar's sextet rule[43b,48] and the local molecular symmetry. A more precise and detailed crystallographic study on HBC was conducted by Herndon and co-workers[51] on HBC **(15)** crystals grown from molten pyrene using mesitylene as a flux. The study showed that HBC crystallizes in the γ motif and the C-C bond lengths with aromatic sextets ranged from 1.371(2) to 1.403(2) Å. By comparison, the CC bond lengths between aromatic sextets were 1.415(2) to 1.461(2) Å.

The HBC system has a much higher surface area than benzene and this represents the origin of its most important physical feature, the columnar π-stacking (Figure 1.9).[52] HBCs self-assemble in a discotic fashion in solution, the solid state and on surfaces, which allows for the transfer of charge in one dimension. As such, HBCs have tremendous potential in the area of organic compound-based molecular electronics.[53]

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[49] Clar, E.; *The Aromatic Sextet*, John Wiley, London, **1972.**
[50] Robertson, J. K.; Trotter, J. *J. Chem. Soc.* **1961**, 1280-1284.
[51] Goddard, R.; Haenel, M. W.; Herndon, W. C.; Krüger, C.; Zander, M. *J. Am. Chem. Soc.* **1995**, *117*, 30-41.
[52] Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *J. Am. Chem. Soc.* **1999**, 6712-6718.
[53] Wu, J.; Watson, M. D.; Müllen, K. *Angew. Chem.* **2003**, *115*, 5487-5491.

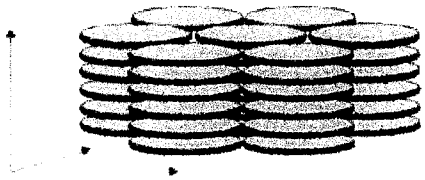

Figure 1.9: Stack type arrangement of HBC molecules.

More specifically, hexabenzocoronenes are found to exhibit significant intrinsic charge carrier mobility for mesogens. Such behavior has brought them an ever-increasing profile in the field of nanotechnology, where discotic liquid crystals are a promising class of materials.[54] Alkylated HBCs are typically used for materials science research because they are soluble and therefore processable.[55] They have been extensively used for the construction of novel nanostructures.[56]

1.5.4 – Synthesis and chemistry

The synthesis of HBCs that was developed by Müllen relies on the oxidative Lewis acid catalyzed cyclodehydrogenation of the hexaarylbenzene derivatives (Scholl reaction *c.f.* **(17)** to **(15)** in Scheme 1.2). The Scholl reaction is capable of forming many aryl-aryl bonds within a single substrate. Müllen has utilized this reaction heavily and provided much of the evidence of just how powerful this reaction is.[47a] The driving force for the cyclodehydrogenation reaction is presumed to be the substantial energy gain (bond energy and aromatic stabilization energy) upon going to a planar PAH system from an oligophenylene precursor.[57]

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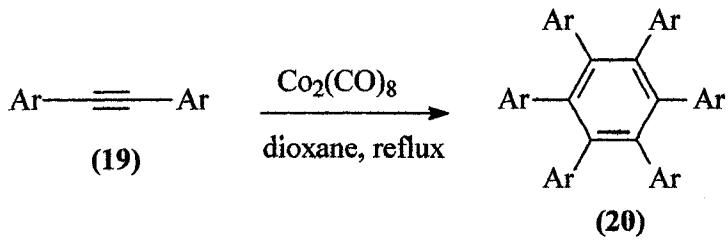
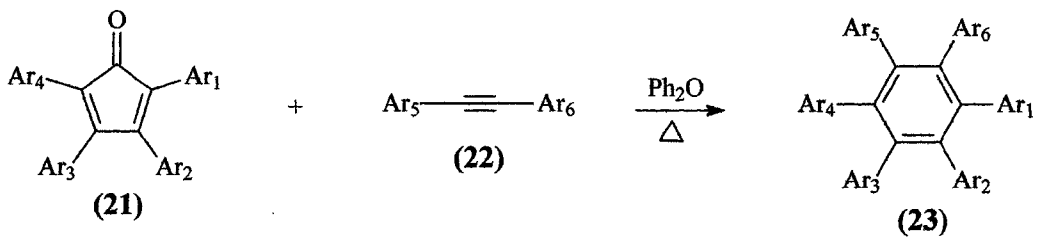
[54] Pisula, W.; Kastler, M.; Wasserfallen, D.; Pakula, T.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 8074-8075.
[55] Samori, P.; Simpson. C. D.; Müllen, K.; Rabe, J. *Langmuir* **2002**, 18, 4183-4185.
[56] Piot, L.; Marchenko, A.; Wu, J.; Müllen, K.; Fichou, D. *J. Am. Chem. Soc.* **2005**, *127*, 16245-16250.
[57] Müller, M.; Iyer, V.; Kübel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1607-1610.

Sixfold symmetric hexaarylbenzene systems are easily prepared by the $Co_2(CO)_8$-catalyzed cyclotrimerization of symmetrical diarylacetylenes[58] (Scheme 1.3). Such systems are conveniently prepared using the Sonogashira reaction. Unsymmetrical diarylacetylenes (*i.e.* where the two aryl groups are different) give mixtures of isomers upon cyclotrimerization.



Scheme 1.3: Cyclotrimerization of the diarylacetylenes to give hexaarylbenzenes.

For the synthesis of hexaarylbenzenes (and HBCs) with lower symmetry (*i.e.* the aryl groups in **(20)** are not all the same), a Diels-Alder cycloaddition between a tetraarylcyclopentadienone **(21)** and a diarylacetylene is generally employed.[54] (Scheme 1.4).

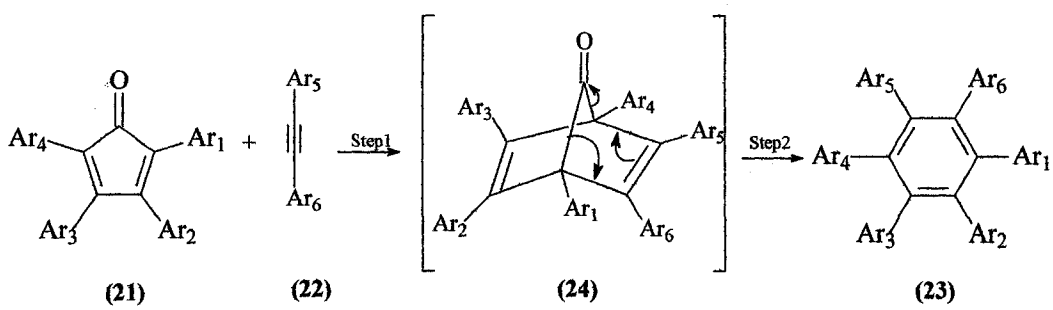


Scheme 1.4: Diels-Alder cycloaddition methodology to give hexaarylbenzenes.

In general, the formation of a hexaarylbenzene in the reaction of tetraarylcyclopentadienone and a diarylalkyne can be explained by a [4+2]

[58] Fechtenkötter, A.; Tchebotareva, N.; Watson, M.; Müllen, K. *Tetrahedron* **2001**, *57*, 3769-3783.

cycloaddition to give a norbornadienone intermediate (**24**) (Scheme 1-5) that suffers chelotropic elimination of carbon monoxide. The formation of a new aromatic ring provides a strong energetic incentive for the loss of CO.



Scheme 1-5: Presumed mechanism for the Diels-Alder reaction.

As noted above, a wide range of HBC systems have been synthesized using the Scholl reaction. These include dyads (*e.g.* (**25**)),[59] water soluble HBCs (**26**),[60] nonplanar persubstituted HBC[61] and a star-shaped heptamer.[62] Even a hexabenzocoronenophane (**27**) has been reported.[63] Some hexabenzocoronenes have been utilized in building nanostructures[64] and controlled nanotubular self-assembly[65] (Figure 1.10).

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[59] Wu, J.; Qu, J.; Tchebotareva, N.; Müllen, K. *Tetrahedron Lett.* **2005**, *46*, 1565-1568
[60] Wu, J.; Li, J.; Kolb, U.; Müllen, K. *Chem. Commun.* **2006**, 48-50.
[61] Wang, Z.; Dötz, F. Enkelmann, V.; Müllen, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1247-1250.
[62] Zhi, L.; Wu, J.; Müllen, K, *Org. Lett.* **2005**. *7*, 5761-5764.
[63] Watson, M. D.; Jäckel, F.; Severin, N.; Rabe, J. P.; Müllen, K. *J. Am. Chem. Soc.* **2004**, 126, 1402-1407.
[64] Jin, W.; Fukushima, T.; Kosaka, A.; Niki, M.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 8284-8285.
[65] Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 13934-13935.

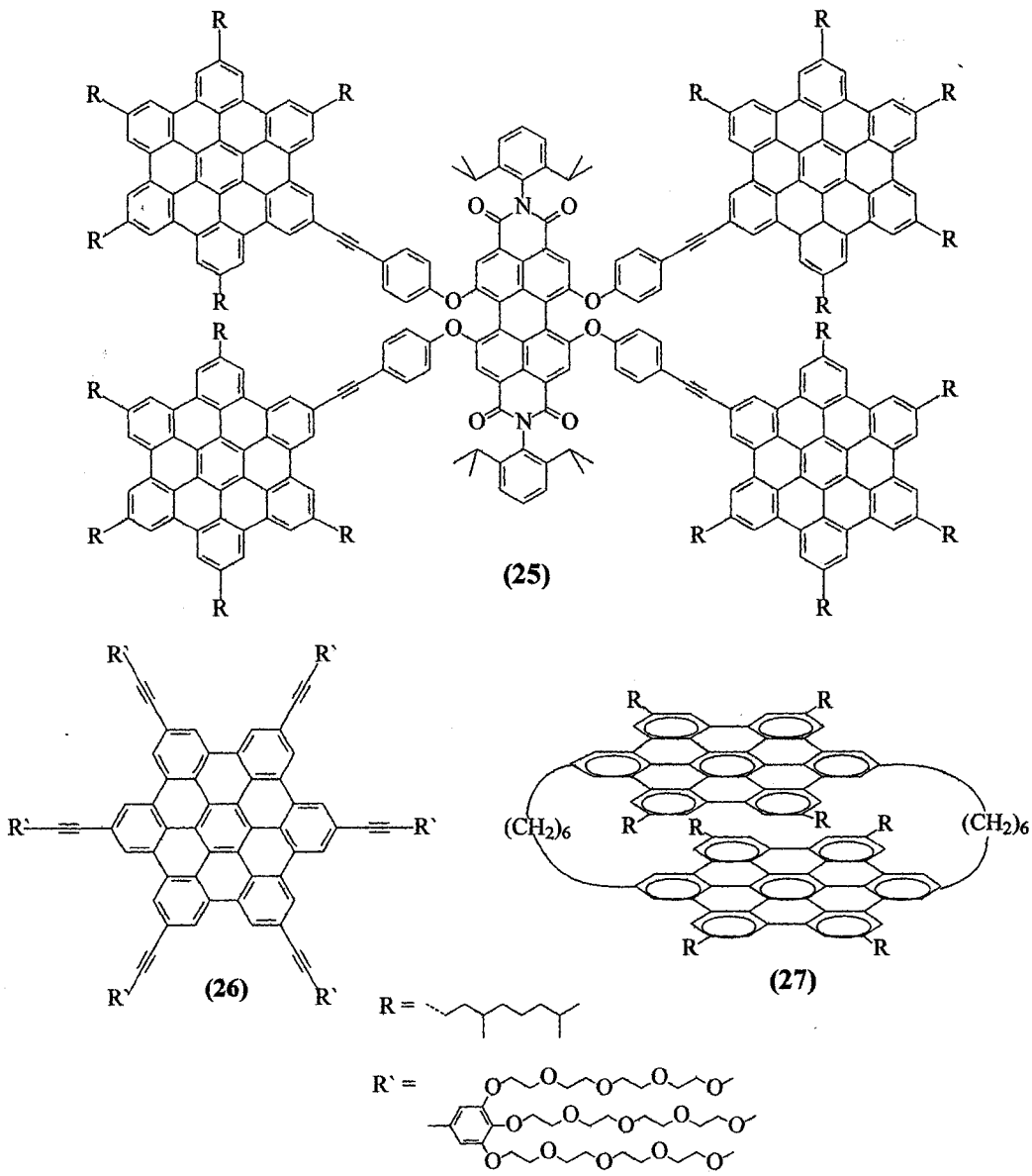

Figure: 1.10: Examples of HBC-containing compounds.

It is noteworthy that the overwhelming majority of synthetic work related to HBC ends with the Scholl reaction. In other words, HBCs are, in most cases, the synthetic target. Very little synthetic work has been done on HBCs following the generation of the HBC unit. Other than some Pd-catalyzed cross-coupling reactions (*e.g.* in the synthesis of **(26)**), this usually involves modification of a part of the

molecule well removed from the HBC system. The use of HBCs as substrates for further synthetic work is an area that is open for development.

1.6 - Nonplanar PAHs in cyclophanes, molecular bracelets and molecular belts.

1.6.1 - Aromaticity and nonplanarity

Ever since Kekulé's proposed structure[66] for benzene was verified experimentally and generally accepted by the chemical community,[67] planarity has, at the very least, been closely associated with aromatic compounds as a class. Indeed, for many years, introductory textbooks listed planarity as a criterion for aromaticity. The clear implication is that nonplanar systems must be nonaromatic. Consequently, without the benefit of any discussion of the effect of deviation from planarity on aromaticity, a large proportion of several generations of chemists developed deeply rooted misconceptions about both the rigidity of aromatic compounds and the relationship between aromaticity and nonplanarity. The notion that aromatic compounds are inflexible and that aromaticity decreases sharply with nonplanarity are still prevalent despite mounting and compelling theoretical and experimental evidence to the contrary (see below).

Computational studies by Wynberg[68] and Lipkowitz[69] concluded that benzene is in fact not very rigid. Lipkpwitz's calculations indicated that distorting benzene away from its lowest energy (planar) conformation is about costly energetically as distorting cyclohexane (which most chemists would considered to be very flexible)

---

[66] a) Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: new york, **1964**. b) Hopf, H. *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2002**. c) Skolink, H.; *J. Chem. Doc.* **1967**; *7*; 185. d) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: London, UK, **1991**.
[67] Balaban, A. T.; Schleyer, P. R.; Rzepa, H. S.; *Chem. Rev* **2005**, *105*, 3436-3447.
[68] Wynberg, H.; Nieuwpoort, W. C.; Jonkman, H. T. *Tetrahedron Lett.*, **1973**, 4623-4628.
[69] Lipkowitz, K.; Peterson, M.; *J. Comp. Chem.* **1993**, *14*, 121-125.

away from its lowest energy (chair) conformation, for low to moderate degrees of distortion.

A computational study by Schaefer on [4]paracyclophane[70] concluded that highly incrementally distorted benzene rings are still aromatic. It wasn't until recently, however, that the effect of nonplanarity on aromaticity was studied for a particular aromatic system as it is distorted from planarity. This was achieved by Bodwell and Cyrañski, who concluded a systematic theoretical and experimental study of the pyrene system, which led to the conclusion that only 10-20% of the aromaticity in the pyrene system is lost in going from the planar conformation to a highly distorted conformation.[71] It follows from this that unusual reactivity in nonplanar aromatics is a consequence of strain relief and not a consequence of diminished aromaticity. Recent editions of many introductory organic chemistry text books still do not address the advanced concepts discussed above (and nor should they), but the language used to introduce the very fundamental and very complex subject of aromaticity is now (as it should be) less rigid than it used to be.

1.6.2 - Nonplanar aromatic compounds

Compounds containing nonplanar systems have been known for decades. Indeed it was the existence of such compounds that provided fuel for the long-lasting debate about the effect of nonplanarity on aromaticity, not to mention the even more heated debate about what exactly aromaticity is.

Nonplanarity in an aromatic system necessarily implies the presence of strain, the amount of which increases with the degree of distortion from planarity.

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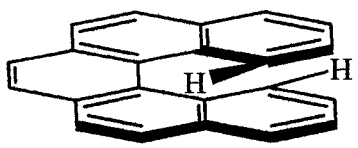
[70] Ma, B.; Sulzbach, H. M.; Remington, R. B.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 8392-8400.

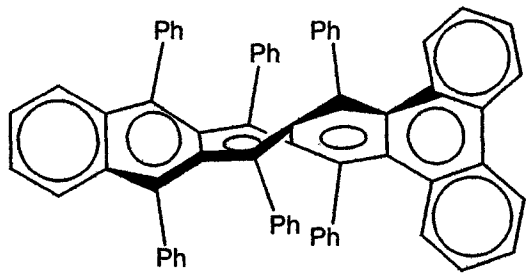
[71] Bodwell, G. J.; Bridson, J.; Cyrañski, M. K.; Houghton , T. J.; Kennedy, J. W. J.; Krygowski, T. M.; Mannion, M; Miller, D. O.; *J. Org. Chem.* **2003**; *68*, 2089-2098.

Consequently, the synthesis of severely distorted aromatic systems is generally challenging. As described by Hopf[64b] the nonplanarity in virtually all known nonplanar aromatic systems arises from one (or more) of only three effects, *i.e.* nonbonded interactions (steric effects), the presence of non-six-membered rings in a polycyclic system (PAH architecture) and/or the bridging of non-adjacent positions (cyclophanes).

In [5]helicene **(28)**, the adoption of a nonplanar conformation would require non-bonded parts of the molecule to occupy the same space. Distortion of the molecule into a helical conformation relieves the repulsive nonbonded interaction, but is accompanied by an increase in stain. The lowest energy conformation reflects the point at which two or more unfavorable effects balance one another. The twisted acenes reported by Pascal[72] (*e.g.* **(29)**) also owe their nonplanarity to non-bonded interactions.



(28)



(29)

The presence of non-six-membered rings in a PAH can cause the system to have a lowest energy conformation that is nonplanar. In such systems, the adoption of a planar conformation would require either several bonds to either elongate or shorten. Bond length deformation is much more costly in energy than bond angle deformation (in this case pyramidalization), so the molecule puckers into a nonplanar

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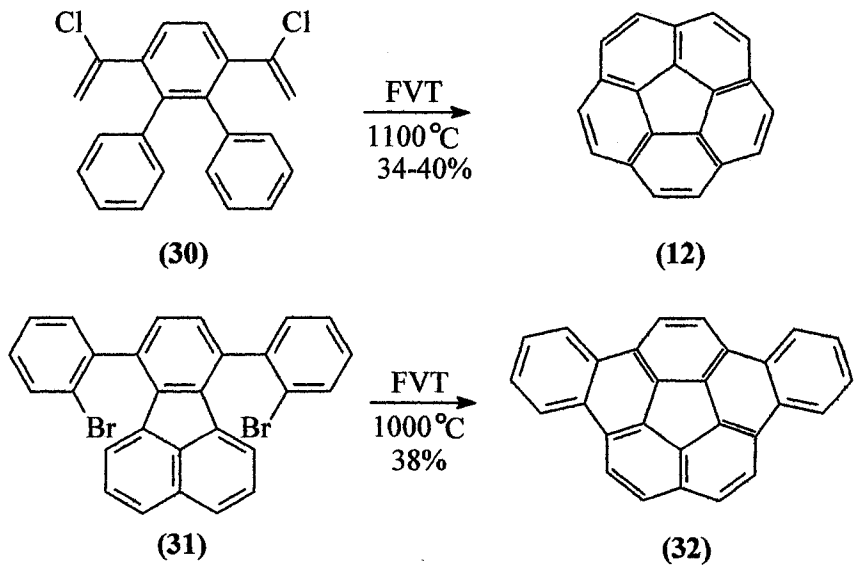
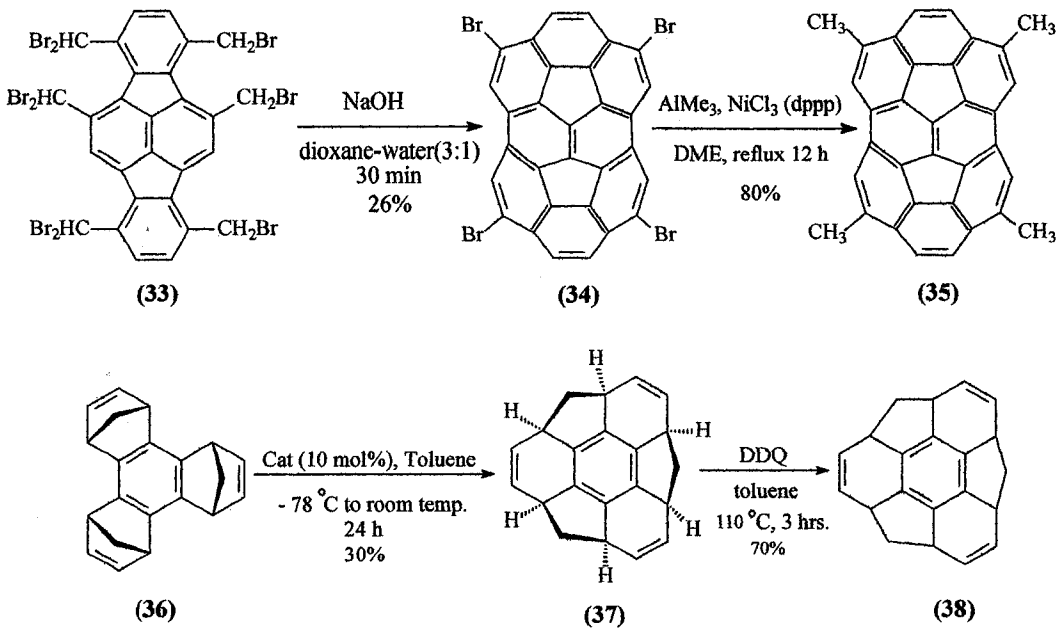
[72] a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652-5653. b) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660-4665.

conformation. When the non-six-membered ring(s) is/are five membered, a bowl-shaped conformation is adopted. Such systems are often referred to as Buckybowls, because of their homology to the fullerenes. Many Buckybowls have been synthesized,[73] many of them under very forcing conditions (FVT at 900-1100 °C). A classic example is corannulene **(12)**, which can be prepared by FVT of bis(chloroalkene) **(30)** at 1100 °C. A variety of non-pyrolytic syntheses of Buckybowls has also been reported[74] (e.g. **(32)** from **(31)**), but these nevertheless typically require a significant input of energy to generate nonplanar skeleta[75] (Scheme 1.6), (Scheme 1.7).



Scheme 1.6: Examples of synthesis of corannulene by FVT.

[73] a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T. Warren, H. B. *J. Am. Chem. Soc.* 1991, *113*, 7082-7083. b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc,* **1992**, *114*, 1920-1921. c) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427-1430.
[74] a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800-7803. b) Xu, G.; Sygula, A.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron Lett.* **2000**, *41*, 9931-9934. c) Sygula, A.; Xu, G.; Marcinow, Z.; Rabideau, P. *Tetrahedron* **2001**, *57*, 3637-3644.
[75] a) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878. b) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580-11581.



Scheme 1.7: Examples of non-pyrolytic Buckybowls.

Nonplanarity in Buckybowls is best quantified using the π-orbital axis vector (POAV), which was introduced by Haddon.[76] The POAV analysis depends upon the construction of a vector along which the π-orbital is assumed to lie. The π-orbital axis vector is obtained from the construction shown in Figure 1.11. χ_1, ..., χ_4 are the hybrid orbitals for the hybridization intermediate between sp^2 and sp^3. The colinear χ_1 with the π-orbital axis vector is constructed specifically to make an equal inclination to the edges of the trihedral angle formed by χ_2, χ_3, and χ_4 and also defined to lie along the Z-axis. The angle θ is the inclination angle formed by χ_2, χ_3, and χ_4 with respect to the X, Y plane. POAV angles up to 11.6° have been reported for Buckybowl **(35)**.[77]

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[76] Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137-142.

[77] a) Sygula, A.; Marcinow, Z.; Fronczek, F. R.; Guzei, I.; Rabideau, P. W. *Chem. Commmun.* **2000**, 2439-2440. b) Poater, J.; Fradera, X.; Duran, M.; Solá M.; *Chem. Eur. J.* **2003**, *9*, 1113-1122.

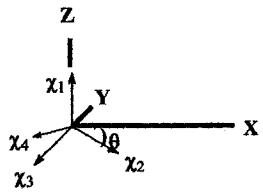
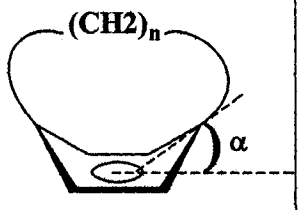


Figure 1.11: POAV in nonplanar conjugated systems introduced by Haddon.

Cyclophanes emerged as a distinct class of compounds in the middle for the 20th century. Today, the field of cyclophane chemistry is very broad and there exists a substantial body of literature on the subject.[66] The simplest cyclophanes consist of one aromatic unit that has a bridge connecting two nonadjacent positions of the arene. The aromatic unit can adopt its preferred planar conformation if the bridge is sufficiently long. However, as the bridge is shortened, the planar conformation would require unfavorable bond lengths and angles in the bridge, so it distorts from planarity. In general, the degree of distortion from planarity (and the molecular strain) increases as the length of the bridge decreases, as exemplified by the [*n*]paracyclophanes (Figure 1.12).

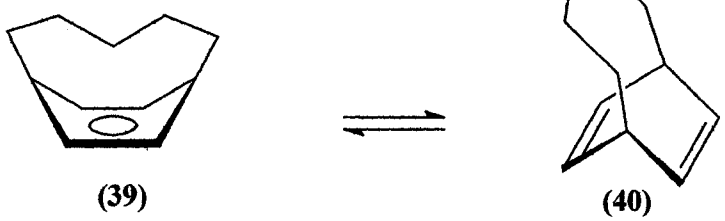
n	α [°]	ΔH_f [kcal mol^{-1}]	$\Delta\Delta H_f$ [kcal mol^{-1}]
15	0.6	-68.2	
14	0.5	-62.3	-5.9
13	1.3	-54.9	-7.4
12	1.9	-48.9	-6.0
11	2.2	-40.5	-8.4
10	3.4	-29.5	-11.0
9	9.6	-18.9	-10.6
8	13.4	-8.7	-10.2
7	16.4	5.1	-13.8
6	22.3	26.2	-21.1
5	28.6	53.8	-27.6
4	35.6	87.8	-34.0
3	79.4	117.8	-30.0



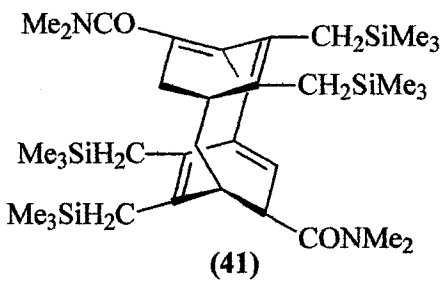
α = deformation angle

Figure 1.12: Deformation angle (α) and heats of formation (ΔH_f) of [*n*]paracyclophanes.

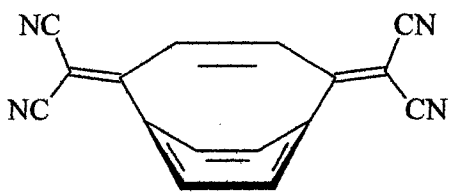
The angle α is a commonly used indicator of the degree of the distortion from planarity in cyclophanes. [6]Paracyclophane[78] is the smallest stable [*n*]paracyclophane. [5]paracyclophane **(39)** exists in equilibrium with its Dewar benzene valence isomer **(40)** and [4]paracyclophane has been proposed as a species with a fleeting existence.[79] Some very distorted benzene units have been generated, such as those in [1.1]paracyclophane **(41)** and the [4]paracyclophane derivative **(42)**. The α angle for these compounds, which are 25.6° and 28.6°, respectively, are the highest ones yet measured.



(39) **(40)**



(41)



(42)

1.6.3 - Pyrenophanes

As implied by the name, pyrenophanes are cyclophanes with one or more pyrene unit(s) as the aromatic component(s). Pyrene **(43)** has ten positions available for substitution. Although mathematically there are 45 pairs of positions that can be

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[78] Kane, V. V.; Wolf, A. D.; Johnes Jr., M. *J. Am. Chem. Soc.* **1974**, 2643-2644.
[79] a) Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F.; *Tetrahedron Lett.* **1974**, 2813-2816. b) Weinges, K.; Klessing, K.; *Chem. Ber.* **1974**, *107*, 1915-1924.

bridged to form a cyclophane, the exclusion of all pairs of adjacent positions (*e.g.* 1,2), all peri-positions (*e.g.* 1,10) and repeats due to symmetry (*e.g.* 1,6 and 3,8 are equivalent) leaves twelve bridging motifs for the pyrene systems. However, only (1,3)- **(44)**,[80] (2,7)- **(45)**, [81] (1,6)- **(46)**,[82] (1,6)(2,7)- **(47)**,[82] (1,8)- **(48)**[82] and (4,9)- **(49)** [83] pyrenophanes have yet been reported, examples of which are shown in Figure1.13.

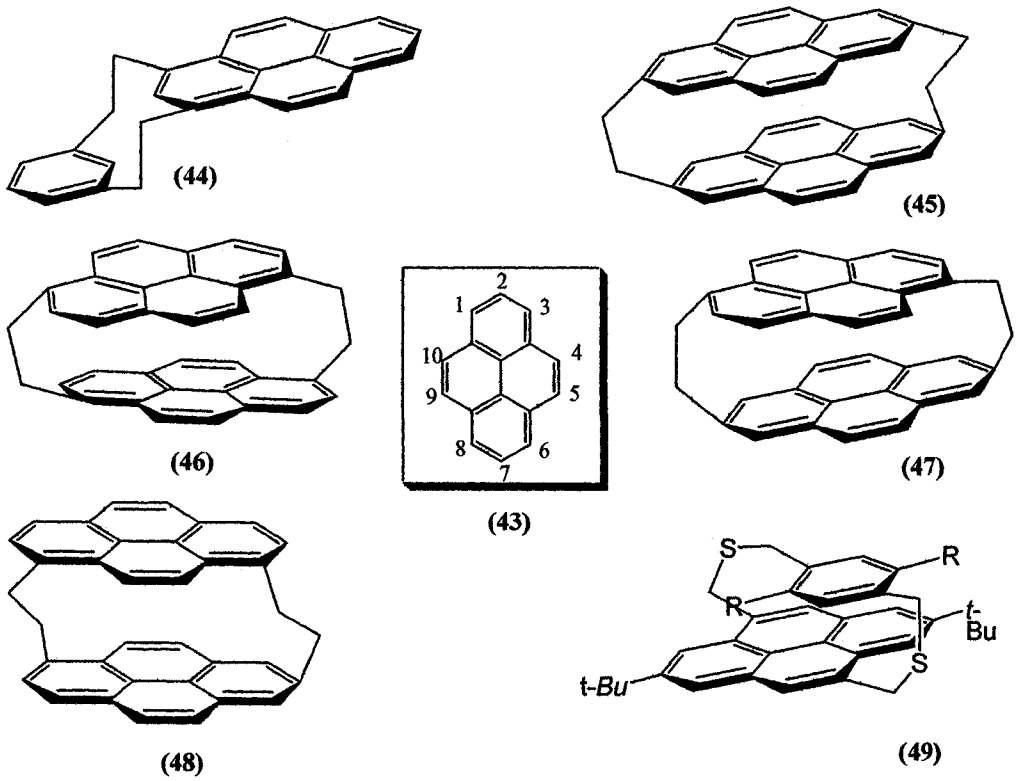


Figure 1.13: Early examples of pyrenophanes.

All of the early examples of pyrenophanes contained two aromatic units. It was not until 1996 that Bodwell reported the first [*n*]pyrenophane *i.e.* 1,8-

[80] Umemoto, T.; Kawashima, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, *7*, 463-466
[81] Umemoto, T.; Satani, S.; Sakata, Y.; Misumi, S. *Tetrahedron* **1975**, *16*, 3159-3162. b) Mitchell, R. H.; Carruthers, R. J.; Zwinkels, J. C. *Tetrahedron Lett.* **1976**, *17*, 2585-2588. c) Irngatin, H.; Kirrstetter, R. G.; Krieger, C.; Rodewald, H.; Staab, H. A. *Tetrahedron Lett*, **1977**, *18*, 1425-1428.
[82] Kawashima, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1978**, *51*, 5115-5118.
[83] Tsuge, A.; Otsuka, M.; Moriguch, T.; Sakata, K. *Org. Bioml. Chem.* **2005**, *3*, 3590-3593.

dioxa[8](2,7)pyrenophane.[84] Since then, several other [*n*]pyrenophanes **(50-55)** and related cyclophanes **(56-60)** have been reported by the same group[71] (Figure 1.14). As with benzene, the pyrene system, which maps onto the surface of various fullerenes (*e.g.* D_{5h} C_{70}), is distorted from planarity by the presence of a sufficiently short bridge and the degree of distortion from planarity increases as the bridge is shortened. The most highly distorted pyrene system yet isolated is 1,7-dioxa[7](2,7)pyrenophane **(50)** $n = 5$), which is more distorted than the pyrene moiety in the equator of D_{5h} C_{70}.

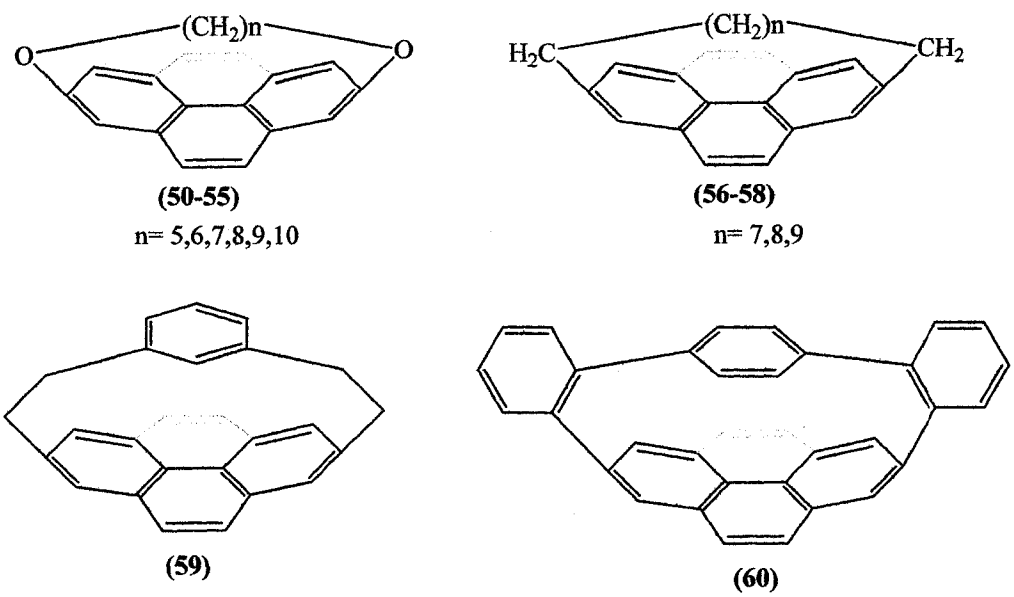
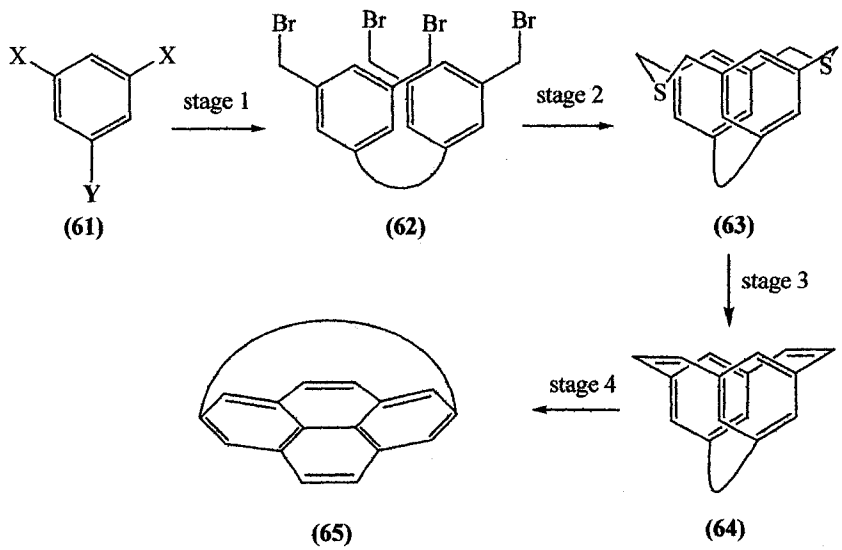


Figure 1.14: Examples of [*n*](2,7) pyrenophanes synthesized by the Bodwell group.

The strategy employed by the Bodwell group for the synthesis of (2,7)pyrenophanes[85,86,87] involves four parts: (1) the tethering of two appropriately

[84] Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, M. R.; Mannion, M. R. *Angew. Chem. Int.* **1996**, *108*, 2280-2281.
[85] Bodwell, G. J.; Bridson, J.; Houghton , T. J.; Kennedy, J. W. J.; Mannion, M. *Chem. Eur. J.* **1999**, *5*, 1823-1827.

substituted aromatic units **(61)** and functional group interconversion to give a tetrabromide **(62)**, (2) the formation of a dithiacyclophane **(63)** (typically using Na_2S/Al_2O_3), (3) conversion of the dithiacyclophane into cyclopentadiene **(64)** using standard cyclophane chemistry and (4) a valence isomerisation/dehydrogenation (VID) reaction to generate the pyrene system. (Scheme 1.8)



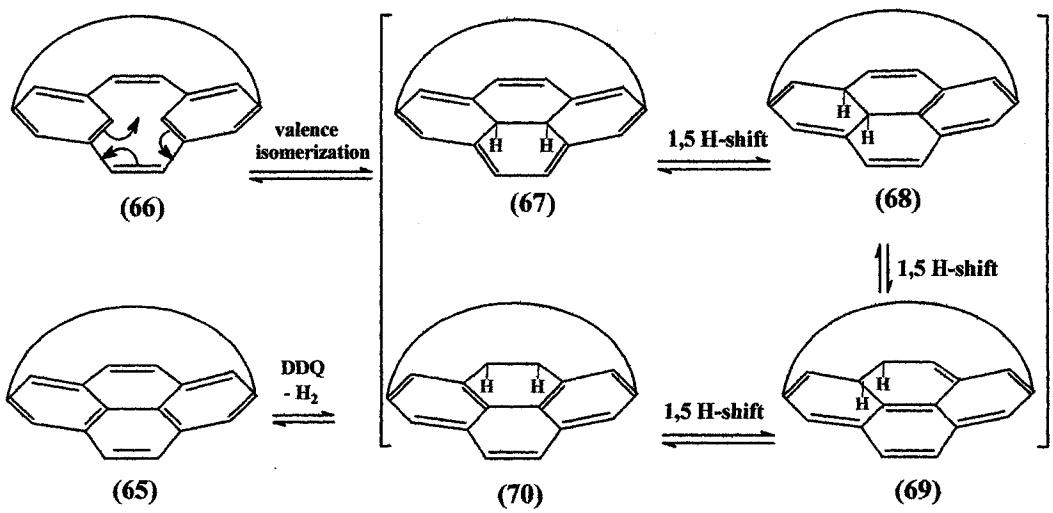
Scheme 1.8: The Bodwell group's strategy for of the synthesis of pyrenophanes.

The key step in this methodology is the one in which the nonplanar aromatic system is generated *i.e.* the VID reaction. There are several noteworthy features in this chemistry. The valence isomerisation is a thermally allowed suprafacial [4*n*+2] π electron electrocyclic ring closing reaction. That this reaction is thermally allowed and not photochemically allowed (*cf.* the stilbene-phenanthrene photocyclization) is a consequence of the *syn* conformation of [2.2]metacyclophanediene **(64)**.[82-86] The product of the valence isomerisation is a *cis*-10b,10c-dihydropyrenophane **(70)**, which

[86] Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2000**, *65*, 5360-5370.
[87] Bodwell, G. J.; Miller, D. O.; Vermeij, R. J. *Org. Lett.* **2001**, *3*, 2093-2096.

upon first examination, was presumed to directly undergo dehydrogenation by DDQ to afford the desired pyrenophane. With the tether of 10 or more atoms, the cyclophanediene reacts under the conditions of its formation to give a mixture of the target pyrenophane **(65)** and rearranged dihydropyrenophane **(70)**. The formation of **(70)** can be explained by a series of three consecutive [1,5]-H shifts. Thus, in cases where the cyclophanediene can be isolated, it may be that [1,5]-H shifts are occurring before dehydrogenation. Whatever the case, DDQ oxidation of any of the dihydropyrenophanes gives the pyrenophane.

Perhaps the most significant feature of this reaction is its power. It has been shown to be capable of delivering very highly distorted pyrene systems under relatively mild conditions (between room temperature and 80 °C). One of the reasons for the ease with which this reaction can give highly strained systems is that conversion of 10b,10c-dihydropyrene into pyrene is accompanied by a substantial decrease in energy.[82-86] As discussed earlier, the pyrene system retains most of its aromaticity upon distortion from planarity, so this driving force is still present, even for highly distorted systems (Scheme 1.9).



Scheme 1.9: Mechanism of the VID process.

The ability to severely bend pyrene using the VID reaction raises the question of whether the bridge in the [*n*](2,7)pyrenophane can be replaced by extended fusion of benzene rings. This would afford a cyclophane system in which the aromatic unit bridges itself *e.g.* **(71)**. Such systems are perhaps better viewed as aromatic belts. The journey from planar pyrene **(43)** to bent pyrenes (*e.g.* **(52)**) to pyrenoid belts such as **(71)** is the big picture within which this work fits. (Figure 1.15)

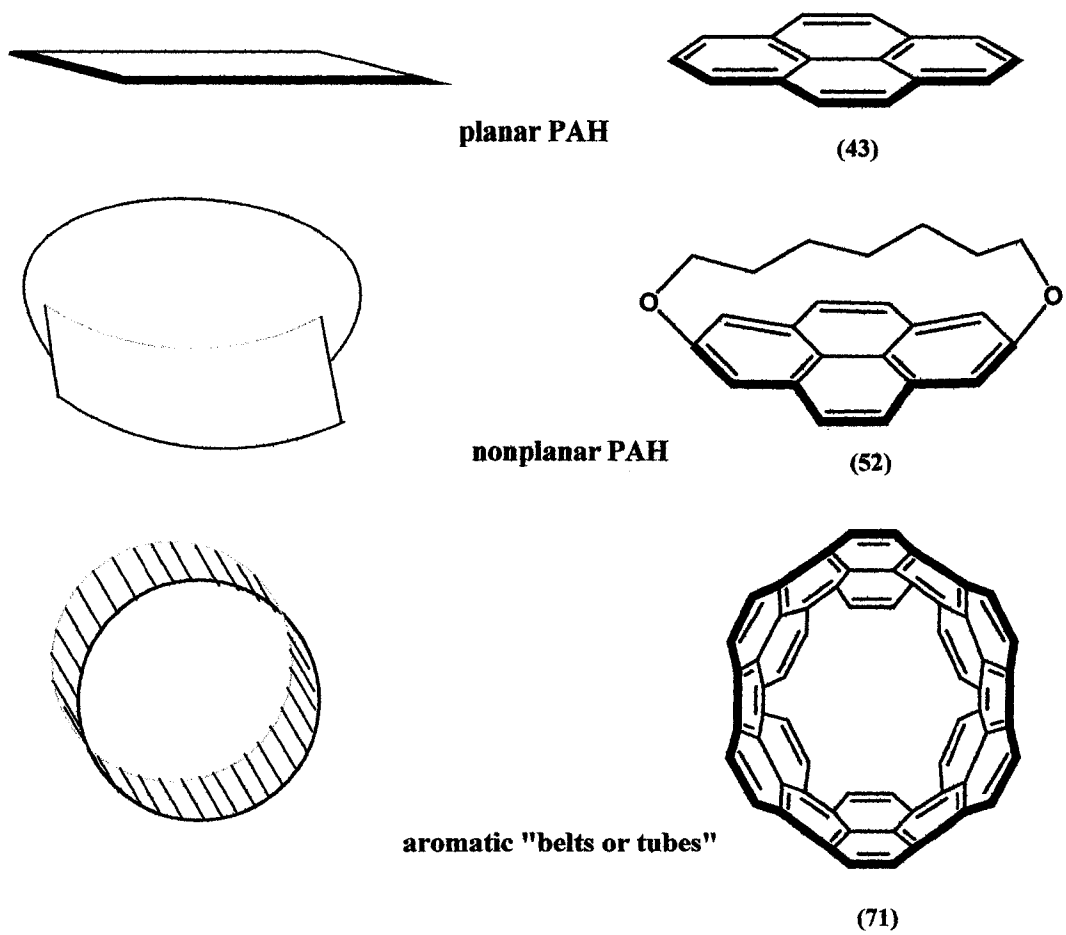


Figure 1.15: Normal aromatics, cyclophanes and belt-like conjugate systems

1.6.4 - Aromatic bracelets and belts

A molecular belt is a macrocyclic system with two multiply connected edges that do not intersect, (Figure 1.16). If the two edges intersect at any point, it is no longer a molecular belt and a term such as "molecular bracelet" more accurately describes the system. For example, cyclodextrins, *e.g.* **(72)**, have edges that intersect at every glycosidic linkage and are best described as molecular bracelets, although they are frequently referred to as being belts, or "belt like". [88] More relevant to this work are aromatic bracelets that, like aromatic belts (see below) have radially oriented p-orbitals. Herges' "picotube" **(73)**[89] and Oda's nanorings **(74)**[90] (also called CPPAs) are noteworthy examples.

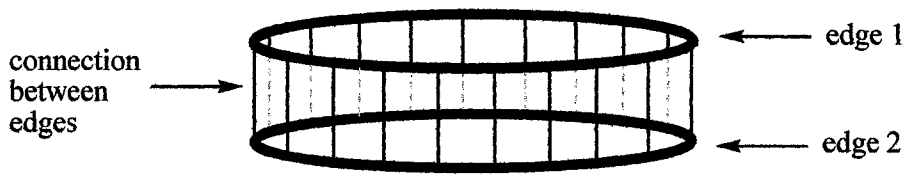
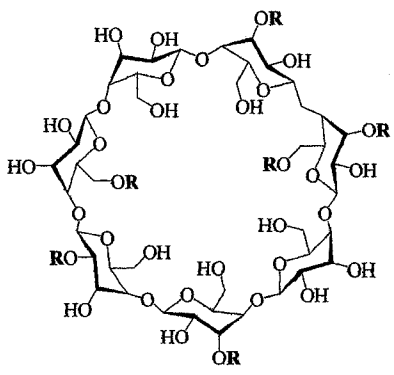
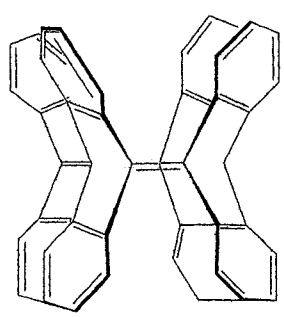


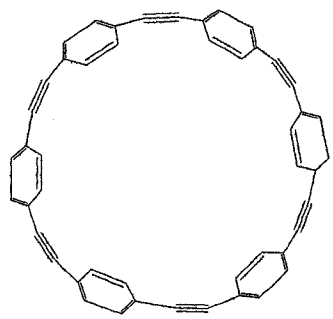
Figure 1.16: Cartoon representation of a molecular belt.



(72)



(73)



(74)

[88] Stoddart, J. F.; *J. Inc. Phen. Mol. Rec. Chem.* **1989**, *7*, 227-245
[89] Treitel, N.; Deichmann, M.; Sternfeld, T.; Sheradsky, T.; Herges, R.; Rabinovitz M. *Angew. Chem. Int. Ed.* **2003**, *42*, 1172-1176.
[90] Kawase, T.; Tanaka, K.; Fujiwara, N.; Darabi, H. R.; Oda, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 1624-1628.

When the surface of a molecular belt consists solely of fused benzene rings, it is referred to as an "aromatic belt". As discussed in more depth below, aromatic belts have been targeted by synthetic organic chemists for decades, dating back to the pre-fullerene era. Indeed, the discovery of the fullerenes and carbon nanotubes conveyed greater significance to aromatic belts, which can be identified on the surface of most fullerenes and can be viewed as nanotubes "slices" or even very short nanotubes themselves.

The homology to carbon nanotubes means that molecular belts can be categorized in the same way as nanotubes, *i.e.* by the roll-up motif. The shortest cross sectional belt-like cut from a zigzag nanotube is belt **(75)**,[66] which is classified as a [*n*]cyclacene. The chiral aromatic belt **(76)** can be assembled by angularly annulating three tetracene units. Finally aromatic belt **(77)** can be excised from an armchair nanotube. This type of belt is called an [*n*]cyclophenacene (Figure 1.17).

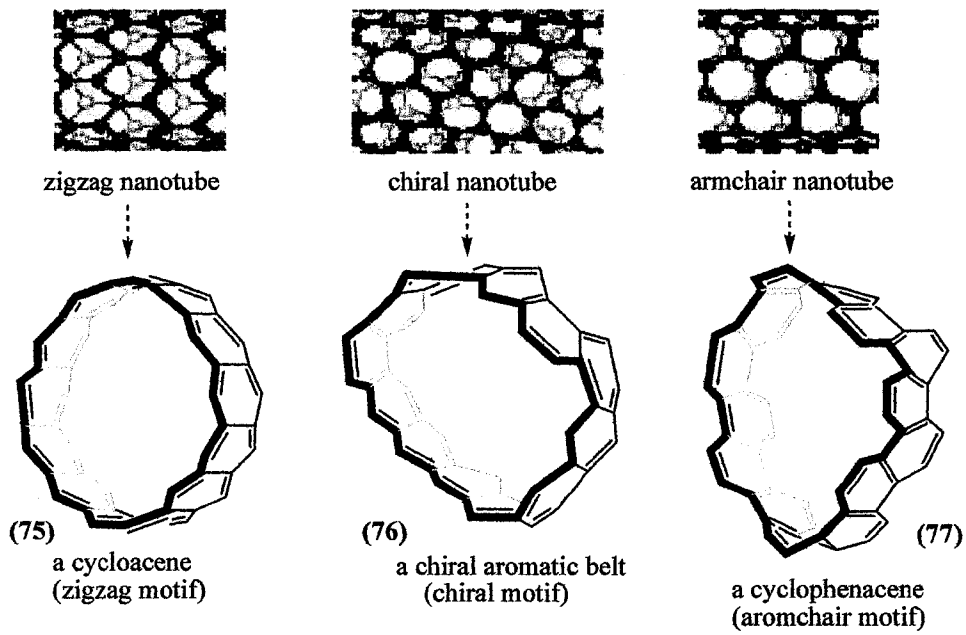
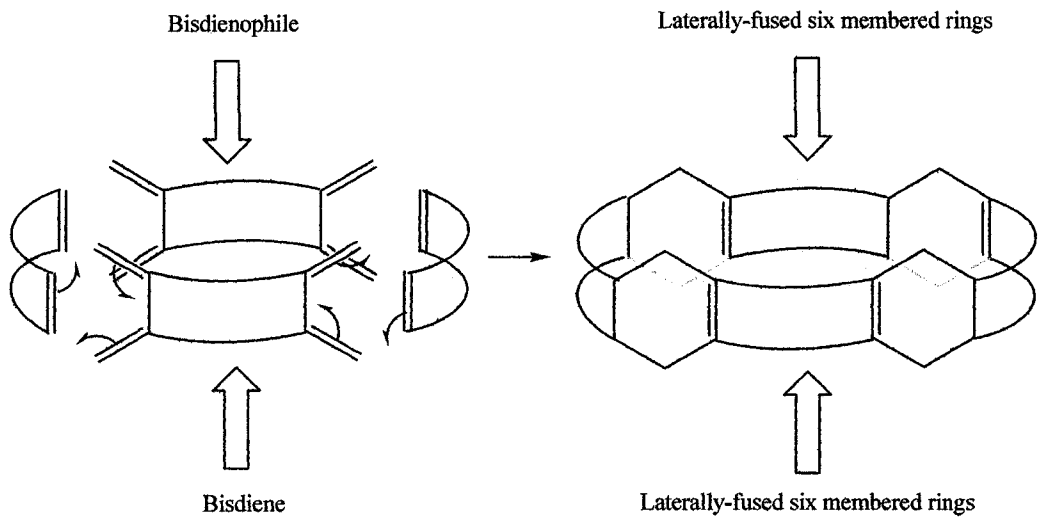


Figure 1.17: Examples of aromatic belts based on the vector notation of the corresponding nanotube.

1.6.5 - Approaches toward aromatic belts.

[*n*]Cyclacenes were first pursued intensively as synthetic targets by Stoddart and colleagues. Their approach relied upon a double Diels-Alder reaction between a bis(diene) and a bis(dienophile) as the key tool for the construction of the required macrocyclic carbon skeleton. (Scheme 1.10).[87]

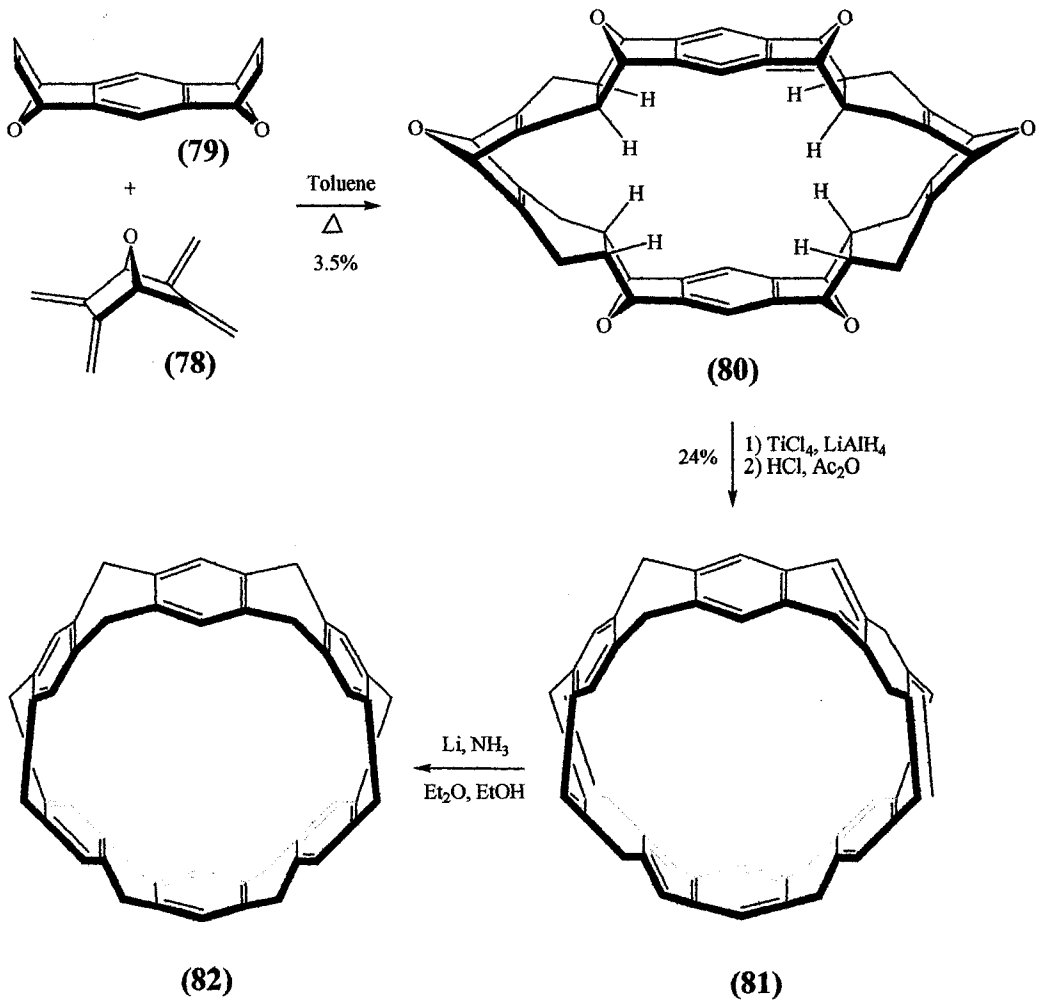


Scheme 1.10: Diels-Alder approach toward the synthesis of a fully aromatic belt by Stoddart.

Bis(diene) **(78)** and bis(dienophile) **(79)** react to give molecular belt **(80)**, in which two molecules of **(78)** and two molecules of **(79)** have been incorporated. Three intermolecular and one intramolecular Diels-Alder reactions, all of which must pass through an *exo* transition state, occur on the path to **(80)**, which was formed (not surprisingly) in very low yield. [91] Reduction of **(80)** was followed by dehydration to afford the partially hydrogenated [12]cyclacene **(81)**. Subjection **(82)** to Birch

[91] a) Ashton, P.; Isaacs, N. S.; Kohnke, F. H. *Angew. Chem. Int. Ed. Eng.* **1988**, *27*, 966-969. b) Kohnke, F. H.; Stoddart, J. F. *Pure Appl. Chem.* **1989**, *61*, 158-1586. c) Mathias, J. P.; Stoddart, J. F.; *Chem. Soc. Rev.* **1992**, 215-225.

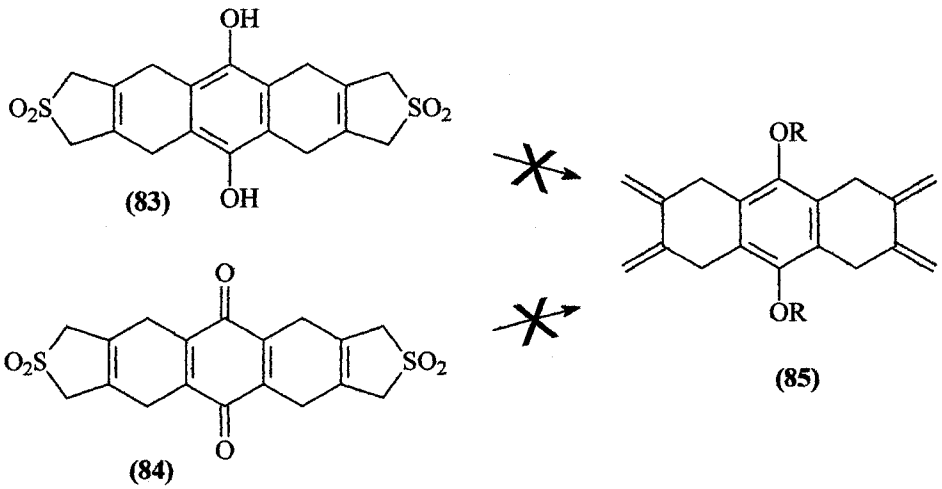
reduction conditions gave a product that was believed to be [12]collarene.[92] Unfortunately, no solid evidence was obtained to confirm the nature of the product. The small quantities of the product and its low solubility prevented further investigation. No subsequent work by Stoddart's group in this area has been reported.



Scheme 1.11: Strategy developed by Stoddart toward [12]cyclacene.

[92] The collarenes are partially hydrogenated [*n*]cyclacenes (*n* must be even) where alternating rings have been hydrogenated on opposite edges of the belt.

Another approach toward cyclacene with the emphasis on a Diels-Alder protocol was planned by Alder, but it also ended with failure.[93] Later on, Paquette *et al.*[94] made another attempt by applying an analogous Diels-Alder approach in an introductory investigation directed towards an aromatic belt/cyclacene synthesis. Unfortunately, such work encountered difficulties due to extreme insolubility of some of the synthetic intermediates (*e.g.* **(80)**.) (Scheme 1.12)



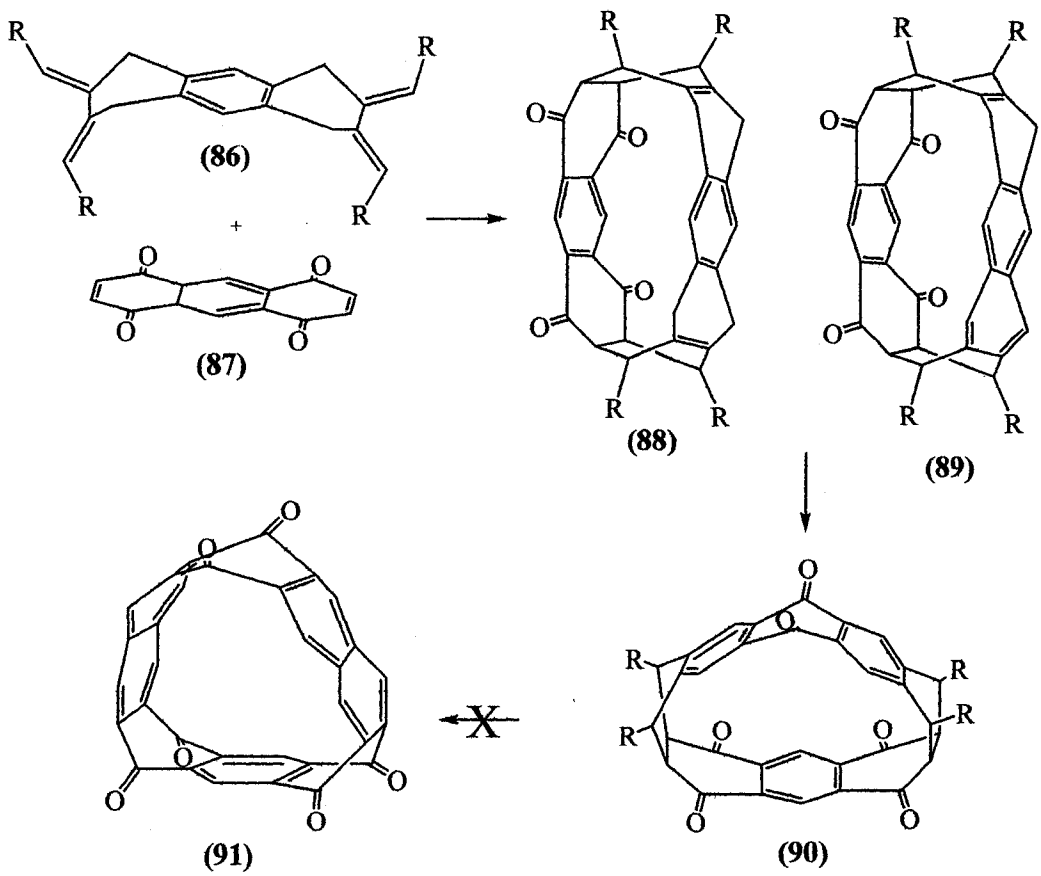
Scheme 1.12: Alder's attempt toward the synthesis of [9]beltene.

Cory's strategy for the synthesis of an aromatic belt also employed the Diels-Alder reaction, but instead of using a rigid bis(diene) and bis(dienophile) like Stoddart, Cory's approach involved the use of a flexible bis(diene) **(86)**. The idea behind this was to allow the diene and the dienophile in the key intramolecular Diels-Alder reaction to more easily find one another.[95] This tactic (Scheme 1.13) proved to be quite successful. For example, the reaction of either **(88)** or **(89)** with pyridinium

[93] Alder, R. W.; Allen, P.; Edwards, L.; Fray, G. I.; Fuller, K.; Gore, P. M.; Hext, N. W.; Perry, M. H.; Thomas, R.; Turner, K. S. *J. Chem. Soc. Perkin Trans. 1* **1994**, 3071-3077.
[94] Graham, R. J.; Paquette, L. A. *J. Org. Chem.* **1995**, *60*, 5770-5777.
[95] Cory, R. M.; McPhail, C. L. *Tetrahedron. Lett.* **1996**, *37*, 1987-1990.

chlorochromate on Celite in benzene under reflux conditions gave anthraquinone cyclophane **(90)** in 35% yield.

Despite having been able to generate synthetically useful amount of some molecular belts with solublizing groups and functionality that could potentially be employed to aromatize them, Cory was unable to prepare any aromatic belt. At least in the case of [8]cyclacene, the strain in aromatic belt may have outweighed the gain in aromatic stabilization energy.



Scheme 1.13: Cory's route to cyclacene derivatives

The stability of the [*n*]cyclacenes may also have been a reason for Cory's failure to generate an aromatic belt. Stoddart commented that the [12]cyclacene should be stable based on the degree of distortion from planarity of each of the benzene rings in comparison to that observed in the benzene rings of the [*n*]paracyclophanes. However, it also bears consideration that the strain-free linear [*n*]acenes become unstable as early as pentacene. If this instability (diradicaloid character) is shared by the strained [*n*]cyclacenes, it can be expected that such compounds will require very careful handling to be generated, isolated and characterized.

Up until 2003, no successful synthesis of an aromatic belt had been reported. In 2003 Nakamura reported[96] the first and only synthesis (Scheme. 1.14) of an aromatic belt to date. Rather than constructing a belt from scratch, these researchers revealed a [10]cyclophenacene that was already present in C_{60} by selective reduction of both the upper and lower caps.

Nakamura's synthesis began with the reduction of C_{60} with an organocopper reagent to give 50 π electron cage compound **(92)** in 92% yield.[97] The original plan was to precede with another copper-mediated multiple addition at the bottom, thereby leaving belt-shaped aromatic system between the now sp^3-hybridized caps. However, this did not take place, presumably due to the presence of the acidic cyclopentadiene hydrogen that was introduced upon quenching the first addition to C_{60}. The acidic proton, which was likely deprotonated by the organocopper reagent, was then "protected" by replacement with a cyano group (63%).

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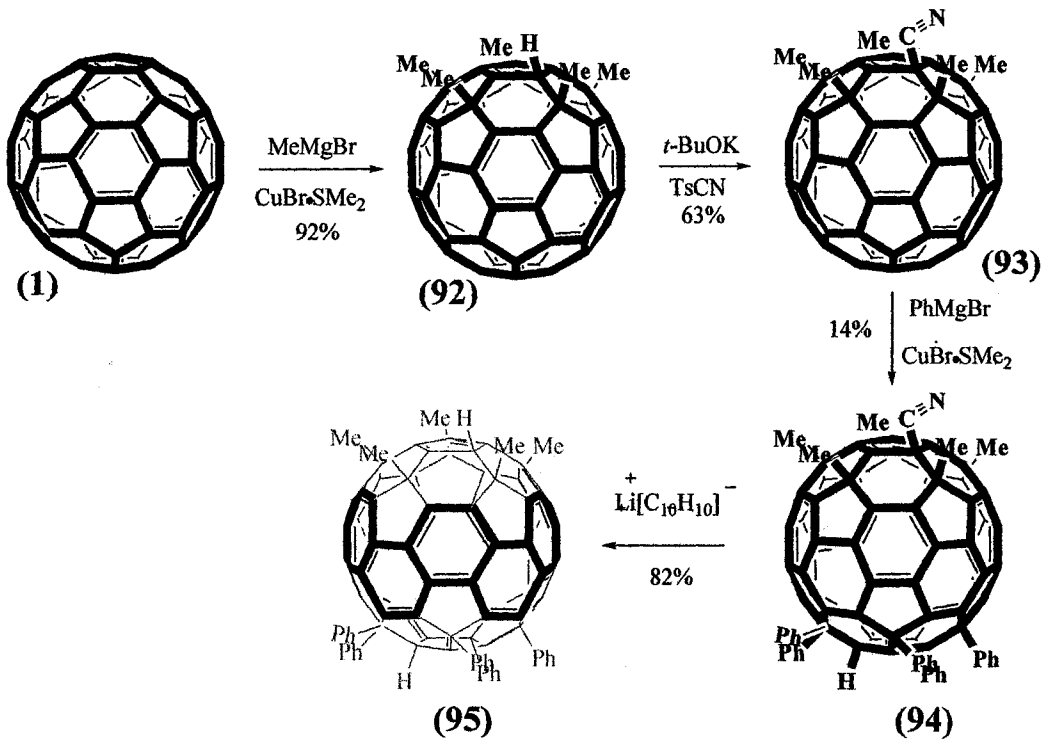
[96] Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2834-2835.
[97] Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 8725-8734.



Scheme 1.14: Synthesis of [10]cyclophenacene by Nakamura *et al.*

With the cyano group in place, fourfold addition of phenyl groups to the lower cap of C_{60} afforded compound **(94)** in 14% yield. The low yield must be viewed in the context of what was achieved. Compound **(94)** contains the first aromatic belt. The final step involved to the synthesis the removal of the "protecting" cyano group, which 40 π electron-aromatic belt **(95)** in 82% yield.

1.7 - Conclusions

Since the discovery of the fullerenes, there has been great interest in the generation of other allotropic forms of carbon. Part and parcel of this has been the quest to achieve rational syntheses not only of fullerenes, but also discrete fragments thereof. Many noteworthy accomplishments have been reported, the most impressive

of which is Scott's synthesis of C_{60}.[98] However, the field remains wide open and this work has the aim of developing rational synthesis of aromatic belts using the VID methodology developed by the Bodwell group for the synthesis of (2,7)pyrenophanes.

[98] a) Boorum, M. M.; vasil'ev, Y V.; Drewello, T.; Scott, L. *Science*, **2001**, *294*, 828-831. b) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500-1503.

Chapter 2

Synthesis of a large Molecular Board

2.1 - The idea

The previous chapter illustrated how the Bodwell group has succeeded in using the valence isomerisation/dehydrogenation (VID) method to prepare [*n*](2,7)pyrenophanes (Figure 2.1). The key features of this chemistry are the ability to impart a high degree of nonplanarity to the pyrene system, the loss of little aromaticity in even the most distorted systems and the relatively mild conditions required to generate such distorted systems.

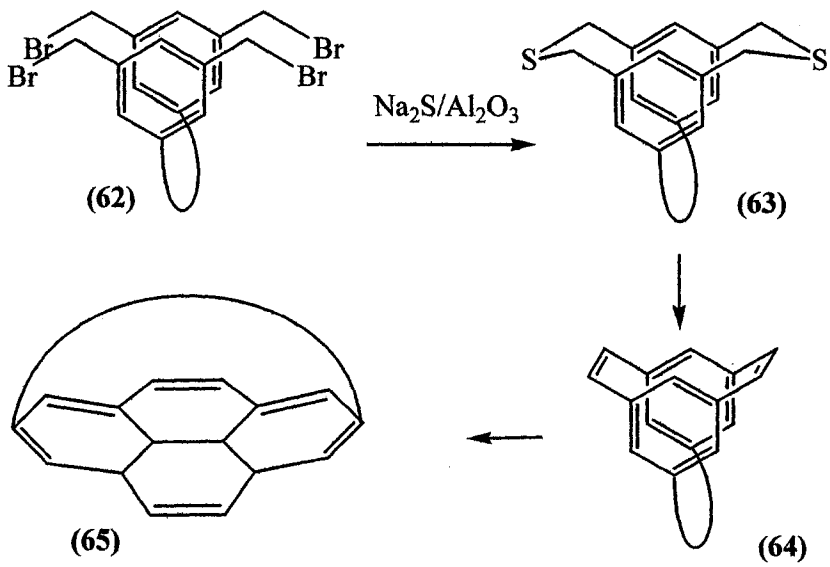
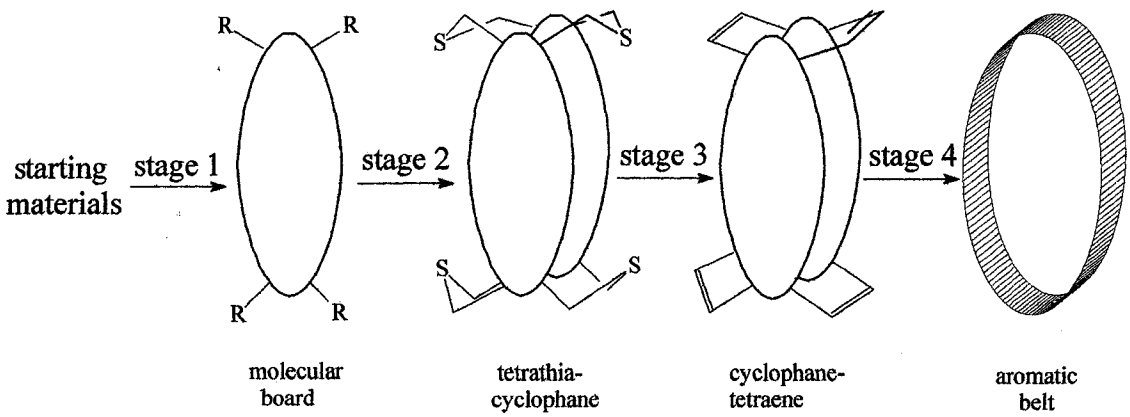


Figure 2.1: Nonplanar PAHs strategy.

The extension of this methodology to the synthesis of aromatic belts has recently been undertaken by the Bodwell group.[97] The general strategy (Scheme 2-1) consists of four stages: (1) the synthesis of an appropriately substituted "molecular board", (2) the union of two boards to form a tetrathiacyclophane, (3) the conversion of the tetrathiacyclophane to a

[97] Yu, H.; M.Sc. thesis, Memorial University, **2005**.

cyclophanetetraene and (4) the application of a double VID reaction to form the belt.



Scheme 2.1: Cartoon representation of the general approach to the synthesis of aromatic belts

Yu[98] attempted to synthesize tetrahydrodibenzo[*a.h*]anthracene-type boards. His synthesis relied heavily on Pd-catalyzed cross-coupling reactions. 4-Bromoisophthalate **(96)** which was prepared from 4-bromo-*m*-xylene in two steps (98%), was converted into diynetetraester **(98)** upon Sonogashira coupling with diyne **(97)**. Catalytic hydrogenation afforded tetraester **(99)**, which was treated with $Br_2/AlCl_3$ to give dibromide **(100)**. A twofold intramolecular Pd-catalyzed direct arylation reaction then afforded molecular board **(102)**. After some optimization work, this reaction could be conducted on 1.17 g of **(100)** to give **(101)** in 91% yield. Tetrabromide **(100)**, which is the required precursor for tetrathiacyclophane formation (stage 2 of the strategy) was obtained upon reduction of **(101)** with DIBAL and treatment of the resulting tetraol **(103)** with concentrated HBr under reflux.

[98] Bodwell, G. J.; Yu, H.; unpublished results.

Unfortunately, neither tetrabromide **(102)** nor tetrathiol **(104)** (prepared from **(103)**) were soluble enough for the use in the cyclophane formation reactions.

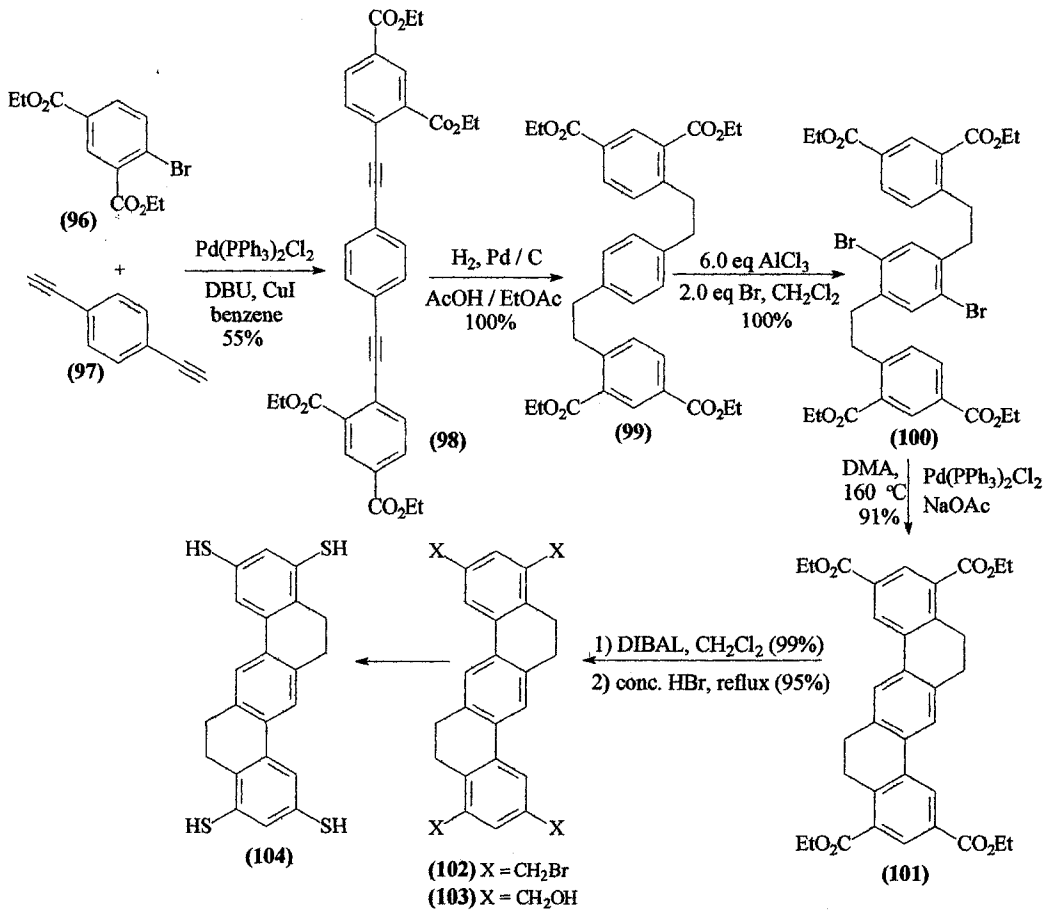
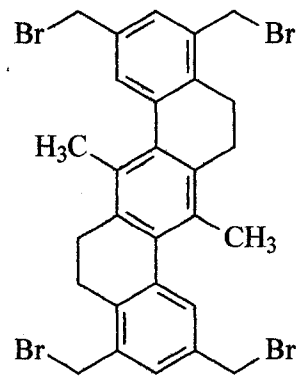


Figure 2.2: Synthesis of tetrahydrodibenzo[*a.h*]anthracene-type boards.

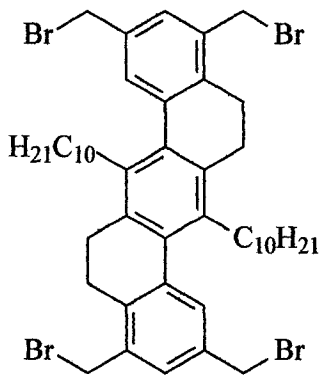
Although Yu did not succeed in progressing past stage 1 of the general strategy, the methodological advances laid the groundwork for related synthetic work, which is currently underway. Using an approach very similar to Yu's, Yao has recently completed the synthesis of tetrabromides **(105)** and **(106)**.[99] Tetrabromide **(105)** is more soluble in chloroform than **(102)**, but still not sufficiently soluble for the ensuing cyclophane chemistry. Tetrabromide **(106)**, on the other hand, is

[99] Bodwell, G. J.; Yao, T. unpublished work.

considerably more soluble than **(102)** and work is underway to convert it into a cyclophane.



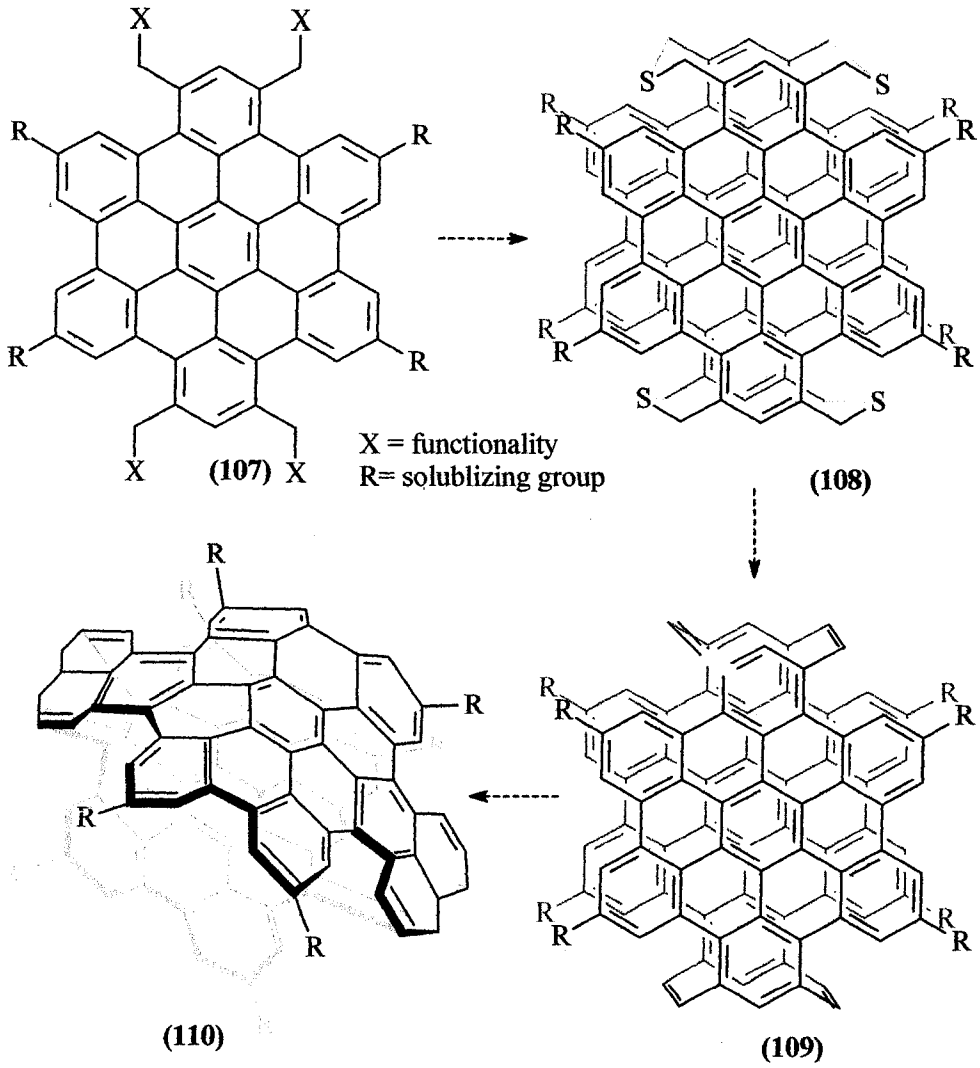
(105)



(106)

The syntheses of **(105)** and **(106)** exceed ten linear steps and have not yet been shown to be amenable to the synthesis of the multigram quantities of the material that would be required for the synthesis of meaningful amounts of the belts. While work in this area continues, an alternative, more concise approach to appropriately substituted, large molecular board was conceived.

Hexabenzocoronene (HBC) **(107)** presented itself as a promising board motif. Subjection of an appropriately substituted HBC molecular board to the general strategy depicted in Scheme 3-2 would give rise to tetrathiacyclophane **(108)**, cyclophanetetraene **(109)** and ultimately belt **(110)**. The key features of HBC **(83)** is that it bears strategically positioned functionality (X) that can be converted into bromomethyl groups and solublizing groups (R) that have the role of maintaining solubility during the subsequent pyrenophane chemistry.



Scheme 2.2: Proposed strategy toward the targeted belt.

2.2 - Retrosynthesis

As shown in Figure 2.3, the synthetic target **(110)** goes back to the cyclophanetetraene **(109)** via the valence isomerisation/dehydrogenation reaction (VID). This will clearly be a crucial transformation. Only at this very late point in the synthesis will it become clear whether the VID reaction is powerful enough to generate the aromatic belt. As discussed previously, there is good reason to believe

that this reaction will be successful. Cyclophanetetraene **(109)** can be brought back to tetrathiacyclophane **(108)** by standard cyclophane methodology,[100] such as the Hoffman elimination and Stevens rearrangement. Disconnection of tetrathiacyclophane **(108)** by thiol/bromide coupling or Na_2S/Al_2O_3[84,85,86] coupling leads back to tetrabromide **(111)**, which could come from functional group interconversion of **(112)** (Scheme 2.4). At this point, the retrosynthesis switches from Bodwell's pyrenophane chemistry to Müllen's HBC chemistry.

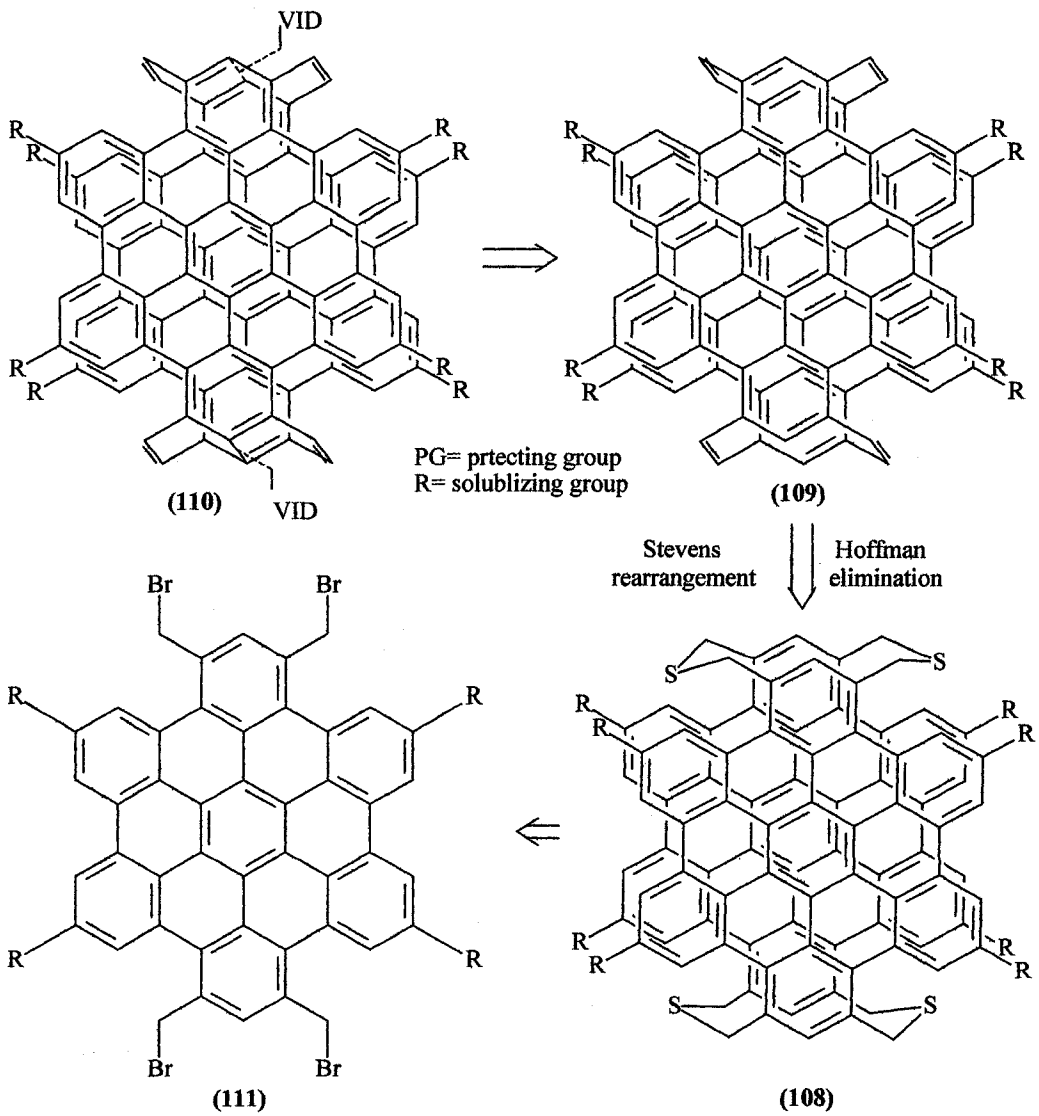


Figure 2.3: Retrosynthetic analysis of the proposed Nanotube.

[100] Mitchell, R. H. *Hetrocycles* **1978**, *11*, 563-568.

A Scholl transform returns HBC **(112)** to hexaarylbenzene **(113)**. This is the expected product of a Diels-Alder reaction between cyclopentadienone **(114)** and diarylalkyne **(115)**. Cyclopentadienone **(114)** arises from the double Knövenagel condensation of the diarylacetone derivative **(116)** and the diketone **(117)**, which also goes back to diarylalkyne **(115)**. The diarylacetone derivative **(116)** is envisioned as coming from phase transfer catalyzed carbonylation of the benzylic bromide **(118)** with iron pentacarbonyl $Fe(CO)_5$. Finally, the acetylene derivative **(115)** is expected to arise from haloarene **(119)** and trimethylsilylacetylene via two Sonogashira reactions (Figure 2.4).

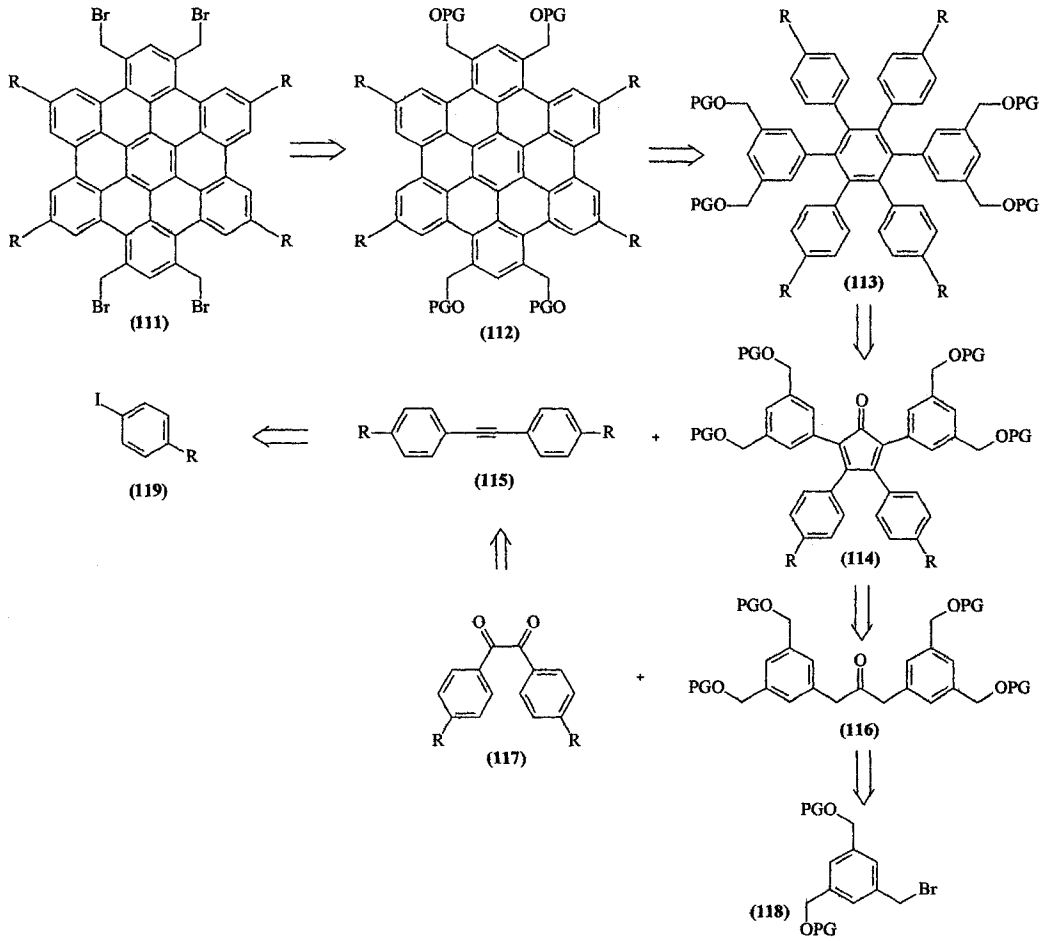
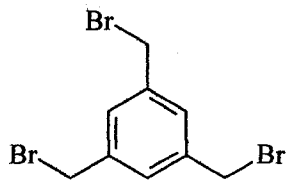


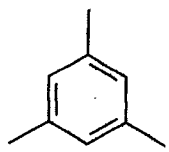
Figure 2.4: Retrosynthetic analysis of the proposed HBC **(111)**.

2.3 -The first synthetic approach

The first approach to the synthesis of a suitably functionalized benzylic bromide involved the synthesis of 1,3,5-tris(bromomethyl)benzene **(120)** and substitution of two of the three benzylic bromides by some sort of an oxygen nucleophile. It has been reported that tribromide **(120)** can be prepared from mesitylene **(121)** by free radical halogenation, albeit in low yields.[101] Because of the direct nature of this approach and the abundance of the starting material, it was chosen for initial work. As expected, the reaction of mesitylene **(121)** with NBS under irradiation with visible light afforded a mixture of brominated products as evidenced by the presence of several singlets at δ 4.44-4.46 in the 500 MHz ^{1}H NMR spectrum of the crude product. However, contrary to the literature report, no conditions could be found that effectively separated the desired product from other products.



(120)



(121)

It is worth mentioning that the literature procedure[102] used CCl_4 as the solvent, where CH_2Cl_2 was used here.[103] The difference in boiling point (40 °C for CH_2Cl_2 and 76 °C for CCl_4) and dielectric constant (2.24 for CCl_4 and 9.08 for CH_2Cl_2) may well have influenced the product ratio to give a mixture that was less

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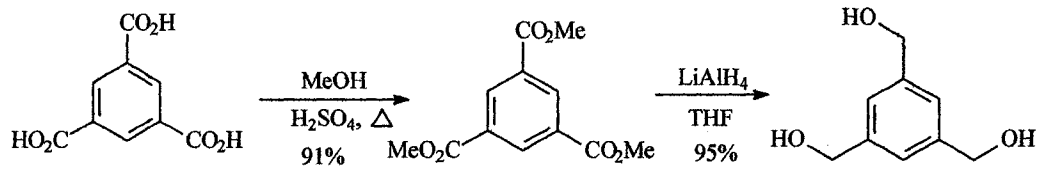
[101] a) Vögtle, F.; Zuber, M.; Lichtenthaler, R. *Chem. Ber.* **1973**, *106*, 717-718. b) Newkome, G. R.; Yao, Z.; Baker, G.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849-850.
[102] a) Shea, K. J.; Stoddard, G. J. *Maromolecules* **1991**, 1207-1209. b) Mitchell, R. H.; Lai, Y-H.; Williams, R. V. *J. Am. Chem.* Soc **1979**, 4733-4735. c) Djerassi, C. *Chem. Rev.* **1948**, 271-314.
[103] Carbon tetrachloride is unavailable in NL.

disposed to the selective crystallization of the desired product. In any event, an alternative synthesis was required.

A longer, but more controlled, route was chosen. Commercially available trimesic acid **(122)** was esterified under Fischer-Speier[104] conditions to afford trimethyl 1,3,5-benzenetricarboxylate **(123)** in 91% yield. This triester was then reduced using lithium aluminum hydride in THF at room temperature to obtain 1,3,5-tris(hydroxymethyl)benzene **(124)** in 95% yield (Scheme 2-4). This compound was insoluble in common organic solvents and was hard to isolate by extraction after quenching. However, it was found that the addition of celite during the quenching step allowed the product to be removed with the celite from the mixture by filtration. The product could then be removed from the celite by washing with large quantities of methanol.



(122) **(123)** **(124)**

Scheme 2-3: synthesis of 1,3,5-tris(hydroxymethyl)benzene 124

Rather than converting triol **(124)** into tribromide **(120)** and pursuing the original strategy, it was decided to try and protect two of the alcohols and then convert the remaining one into a bromide. Unfortunately, other problems were encountered when attempts to doubly protect the alcohol **(124)** (Scheme 2.4) were performed.

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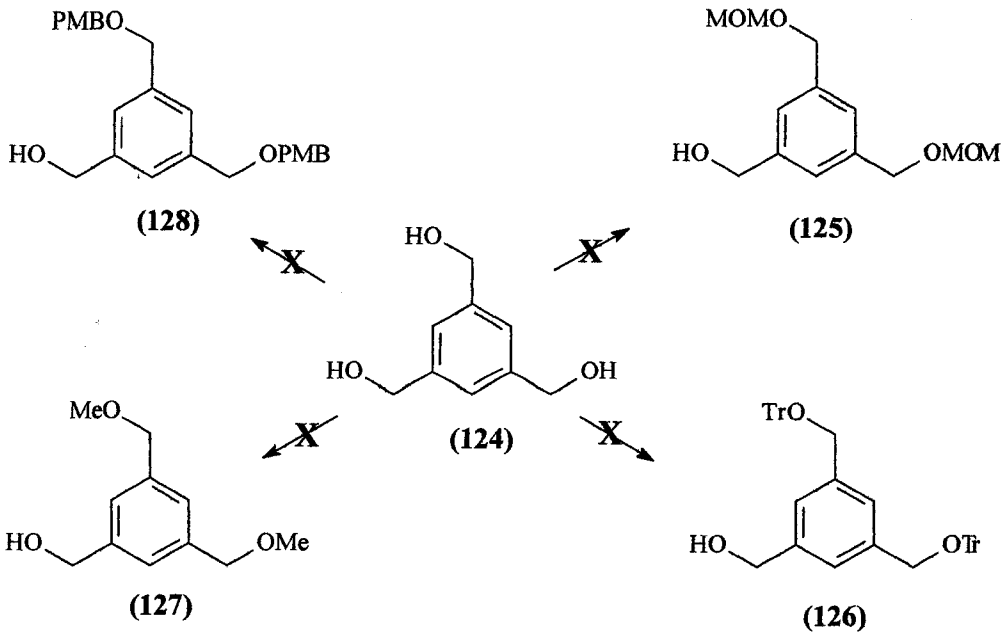
[104] Fischer, E.; Speier, A. *Ber. Dtsch. Chem. Ges.*; **1895**, *28*, 3252-3258.

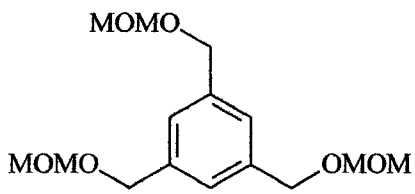


Scheme 2.4: attempted protection of **(124)**.

Entry	Reagent	Solvent	Base
1	MOMCl	THF	NaH
2	MOMCl	DMF	NaH
3	MOMCl	DMF	pyridine
4	TrCl	DMF	Et_3N
5	TrCl	DMF	pyridine
6	TrCl	DMF	NaH
7	CH_3I	THF	NaH
8	PMBCl	THF	Et_3N
9	PMBCl	DMF	pyridine
10	PMBCl	DMF	NaH

Table 2-1: Reaction conditions used for the attempted protection of **(124)**

Attempts to introduce two MOM groups into triol **(124)** where carried under different conditions (Table 2-1). In the first attempt (Entry 1), THF was the solvent of choice, but the reaction did not proceed to any appreciable degree after two days of reaction. The starting material was recovered in 71% yield along with a small amount of a mixture of products that presumably consisted of monoprotected, diprotected and perhaps triprotected products. With the addition of tetrabutylammonium iodide, (Entry 2), the triply protected product **(129)** was isolated was isolated (5-10%) and the rest was unreacted starting material. Such a result indicates that the rate of reaction of a given alcohol increases with the number of MOM groups already present. This is likely due to an increase in solubility (and thus an increase in concentration) with each successive protection and not due to an inherent change in reactivity of the individual OH groups.

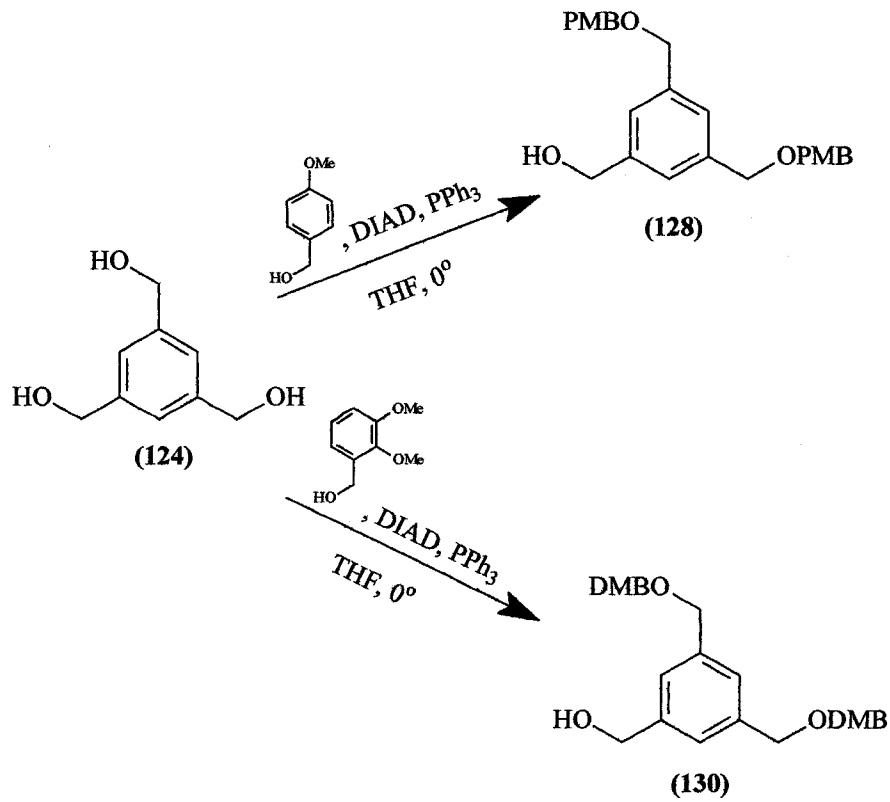


(129)

The use of the trityl (Tr) group was then investigated (Entries 4-6). In each case, the starting material was returned as the major product, although TLC analysis indicated the formation of small amounts of new products that were difficult to separate. The formation of methyl ethers (Entry 7) was then pursued and, like the previous reactions, the results were unsatisfactory. TLC analysis showed the formation of new compounds, but far from complete consumption of the starting material. As before, the new spots were not well separated on the TLC plate. The relatively large volume of THF required to dissolve triol **(124)** may well have been responsible for lowering the rate of the protections. Finally, attempts to introduce

PMB groups were performed (Entries 8-10), but these all had outcomes similar to those described above.

At this point, a decision was made to change the method used in protecting triol **(124)**. Mitsunobu conditions were employed in two different attempts. The first attempt was carried out using two equivalents of *para*-methoxybenzyl alcohol in an attempt to synthesize the doubly protected alcohol **(128)** or **(130)**. Unfortunately, this attempt was unsuccessful and no reaction was observed. In the second attempt, 2,3-dimethoxybenzyl alcohol was used. In this case, several products were formed again with incomplete consumption of the starting material but no TLC conditions could be found under which they were well separable. These reactions presumably failed because *para*-methoxybenzyl alcohol and 2,3-dimethyloxybenzyl alcohol are not sufficiently acidic to participate in the Mitsunobu reaction.

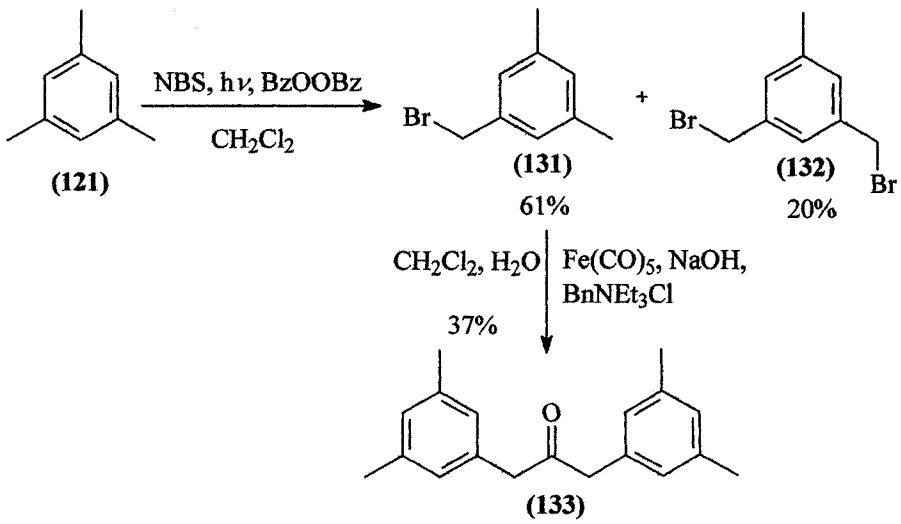


Scheme 2.5: Attempted protection of **(124)** under Mitsunobu conditions.

After these unsuccessful attempts to protect triol **(124)**, it was decided to modify the synthetic plan such that the introduction of the functional groups was postponed to a later stage of the synthesis. This decision was not taken lightly. From a strategic perspective, it would be preferable to install the required functionality at an early stage. The disadvantages of introducing functionality later on using much less abundant materials was weighed carefully against the need to progress beyond the early stages of the synthesis. Although the decision was made in favor of progress, it was recognized that the original strategy would very likely need to be revisited.

2.4 - A modified synthetic approach

The modified approach, like the very first one, began with mesitylene **(121)**. However, the plan was to introduce only one bromine atom to give bromide **(131)**. The use of one equivalent of NBS led to the formation of 1-(bromomethyl)-3,5-dimethylbenzene **(132)** (61%) and 1,3-bis(bromomethyl)-5-methylbenzene **(132)** (20%), which could be separated easily using column chromatography.



Scheme 2.6: Synthesis of 1,3-bis(3,5-dimethylphenyl)acetone.

Furthermore, this reaction was conveniently carried out on up to 26 g of mesitylene. Bromide **(131)** was then subjected to the carbonylation reaction initially reported by Otsuji.[105] 1,3-Bis-(3,5-dimethylphenyl)acetone **(133)** was isolated in 37% yield. The yield was somewhat disappointing, but the reaction could reliably deliver *ca.* 6 g of product per run.

This procedure has been utilized heavily by Müllen[106] and colleagues for the synthesis of numerous 1,3-diarylacetones as HBC precursors. Although the yields can vary greatly, it is perhaps the best method for the preparation of diarylacetone derivatives. Some discussion of this reaction is warranted. It is a phase-transfer catalyzed (PTC) reaction[107] that proceeds under mild conditions. The use of NaOH means that base-sensitive functionality should be avoided. The mechanism of the reaction has been studied by Thilmont,[108] who concluded that two competing mechanistic cycles are in operation (Figure 2-5). Cycle A is responsible for the production of phenylacetate anion and cycle B is responsible for the production of the 1,3-diarylacetone.

After successfully synthesizing **(133)**, the first precursor for the synthesis of the targeted molecular board **(112)**, the synthesis of the other required precursor, the diarylacetylene derivative **(115)** was initiated. Whereas diarylacetone **(133)** introduces the handles (four methyl groups) that will eventually be used for the cyclophane formation, this part of the synthesis is where the four solublizing groups of molecular board **(112)** originate from.

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[105] Kimura, Y.; Tomita, Y.; Nakanishi, S.; Otsuji, Y.; *Chem. Lett.* **1979**, *8*, 321-324.
[106] Ito, S.; Wehmeier, M.; Brand, D. J.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K.; *Chem. Eur. J.*; **2000**, *6*, 4327-4342
[107] Abbayes, H.; Salaün, J-Y. *Dalton Trans.* **2003**, 1041-1052.
[108] Abbayes, H.; Clément, J-C.; Laurent, P.; Tanguy, G.; Thilmont, N. *Organometallics* **1988**, *7*, 2293-2299.

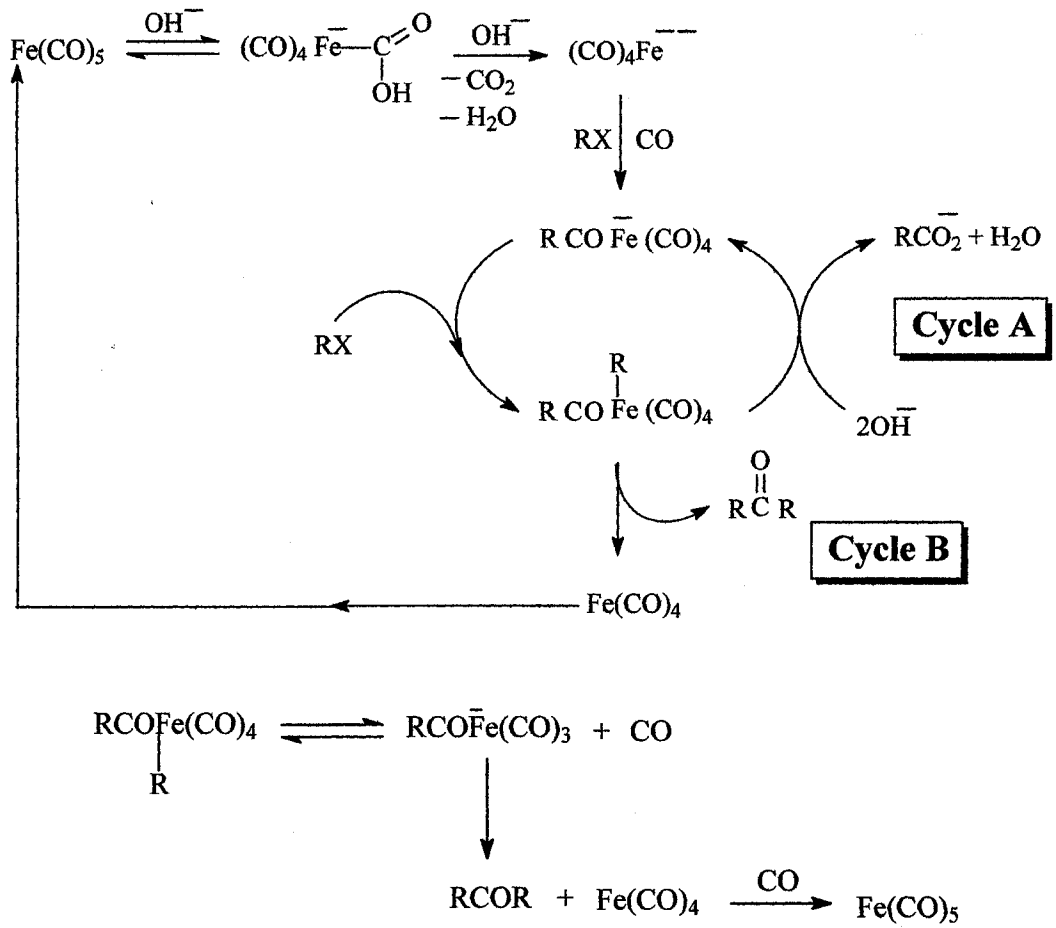
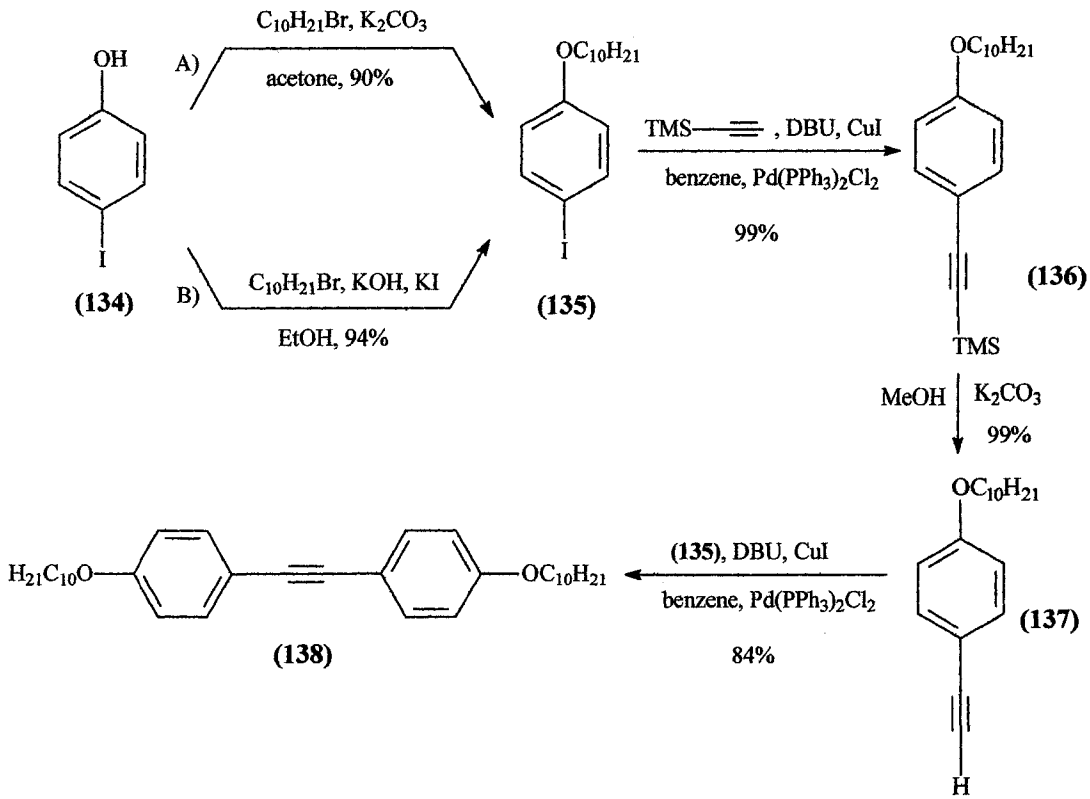


Figure 2.5: The two competing cycles of carbonylation of benzyl bromides under PTC conditions with iron pentacarbonyl. Adapted from ref. 109.

Long alkyloxy groups are common solublizing groups in materials chemistry and methoxy groups have been reported to survive the Scholl reaction. [61,109] Therefore, the decyloxy group was chosen as the solublizing group for initial work. Synthetic work started with commercially available 4-iodophenol **(134)**, which was *O*-alkylated with 1-bromodecane (Scheme 3-9). Two sets of reaction conditions were employed, both of which delivered 1-decyloxy-4-iodobenzene **(135)** in excellent yield. Owing to a more convenient work-up, reaction B (Scheme 3.9) was the method

[109] Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, C. H. *Angew. Chem. Int. Ed.* **1999**, *38*, 3748-3752.

of choice. Iodide **(135)** was then subjected to Sonogashira coupling with trimethylsilylacetylene, which afforded alkyne **(136)** in nearly quantitative yield. Efficient priotodesilylation of **(136)** was achieved using K_2CO_3/MeOH and the resulting terminal alkyne **(137)** was used in another Sonogashira reaction with iodide **(135)**. This afforded bis(4-decyloxyphenyl)acetylene **(138)** in 84% yield.

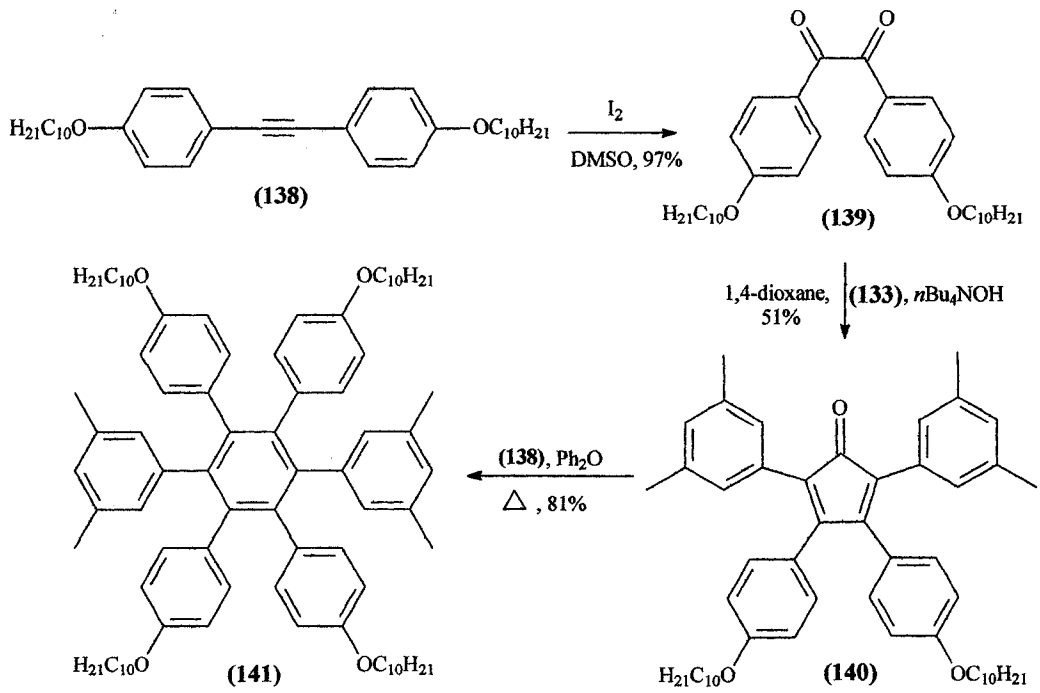


Scheme 2.7: Synthesis of 4,4'-bis(decyloxyphenyl)benzene **(138)**.

Diarylalkyne **(138)** was not only ready for use as a dienophile for the forthcoming Diels-Alder reaction, but it also served as a precursor to one of the building blocks of the diene it was slated to react with. Treatment of **(138)** with iodine in DMSO[110] resulted in the formation of diketone **(139)** in 97% yield. Double

[110] a) Yusybov, M. S.; Filimonov, V. *Synthesis*, **1991**, 131-132. b) Yusubov, M. S.; Krasnokutskaya, E. A.; Vasilyeva, V. P.; Filimonov, V. D.; Chi, K-W. *Bull. Korean Chem. Soc.* **1995**, *16*, 86-88. c) Yusubov, M. S.; Zholobova, G. A.; Filimonova, I. L.; Vasil'eva, V. P.; Filimonov, V. D.; Chi, K-W. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1051-1055.

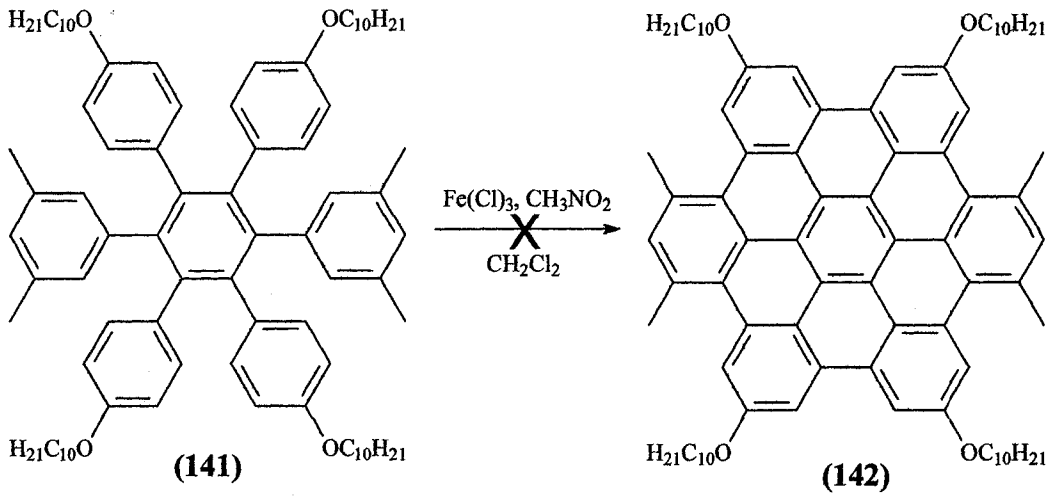
Knövenagel condensation of diarylacetone **(133)** with diketone **(139)** then gave rise to tetraarylcyclopentadienone **(140)** (51%) as a deep maroon, tarry substance. The yield was a little disappointing, but synthetically useful quantities of **(140)** were produced. The isolation of **(140)** as a non-solid material indicated that the solublizing groups were already doing their job.



Scheme 2.8: Synthesis of hexaarylbenzene derivative **(141)**.

The stage was now set for the Diels-Alder reaction between **(138)** and **(140)** to give hexaarylbenzene **(141)**, which is the projected precursor of the targeted board **(142)**. Formally, this is an inverse electron demand Diels-Alder (IEDDA) reaction because the diene **(138)** is electron deficient and the dienophile **(140)** is electron rich. In the case at hand, reaction of **(138)** and **(140)** in diphenyl ether (b.p. = 257 °C) at reflux afforded hexaarylbenzene **(141)** (81%) as a sticky, light brown oil. Again, the isolation of the product as a non-solid material was taken as an indication that the decyloxy groups were working well.

$FeCl_3$ in CH_3NO_2/CH_2Cl_2 is a commonly used Lewis acid/solvent combination[111] for the Scholl reaction and it was chosen for the attempted conversion of **(139)** into HBC **(142)**, but, unfortunately, this reaction was not successful (Scheme 2.9).



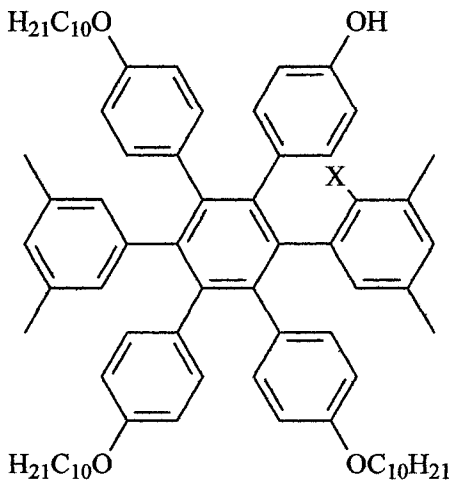
(141) **(142)**

Scheme 2.9: attempted synthesis of molecular board **(140)** by the Scholl reaction

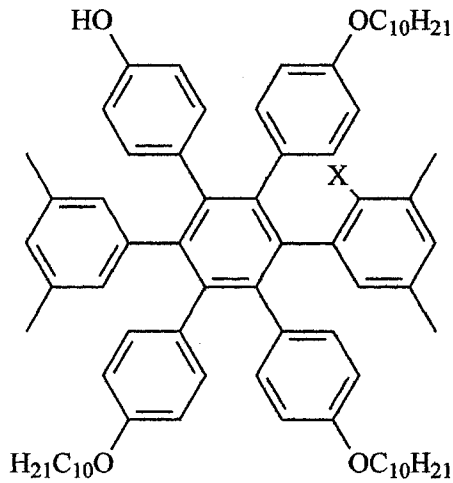
According to TLC analysis, several products were formed. Column chromatography resulted in the isolation of two compounds that were pure by TLC and ^1H NMR analysis. The remainder of material obtained was mixtures of compounds. The first eluted compound was tentatively assigned to either structure **(143)** or **(144)** based on one and two dimensional NMR experiments. The ^1H NMR spectra ($CDCl_3$ and C_6D_6 solutions) were very informative (Figure 2.6). The presence of three OCH_2 signals indicated that one decyl group had been lost and the observation of three CH_3 signals in 1:1:2 ratio indicated that one of the dimethylphenyl groups had undergone a reaction that rendered the two methyl groups

[111] Scholl, R.; Mansfield, J.; *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734-1746.

inequivalent. In the aromatic region, the observation of four separate AA`BB` / AA`XX` systems (more clearly seen with a C_6D_6 solution) unambiguously ruled out the possibility of any cyclodehydrogenation having occurred. Two relatively broad, weakly coupled (1H, ^{1}H-COSY spectrum) singlets in a 1:1 ratio, which was consistent with the monosubtitution of the other 3,5-dimethylphenyl groups at the 2-position. Considering the reaction conditions, the most logical substituent is a chlorine atom. There is some precedent that chlorination can occur during the Scholl reaction.[112] The absence of a signal for a phenolic OH in the IR and ^{1}H NMR spectra are two troubling inconsistencies between the spectra and the proposed structures. Unfortunately, several attempts to obtain a mass spectrum were unsuccessful or inconclusive, so the structural assignment of this product must remain tentative until spectroscopic (and other) data becomes available. In any event, the product was definitely not the desired product.



(143)



(144)

[112] Rempala, P.; Kroulík, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002-15003.

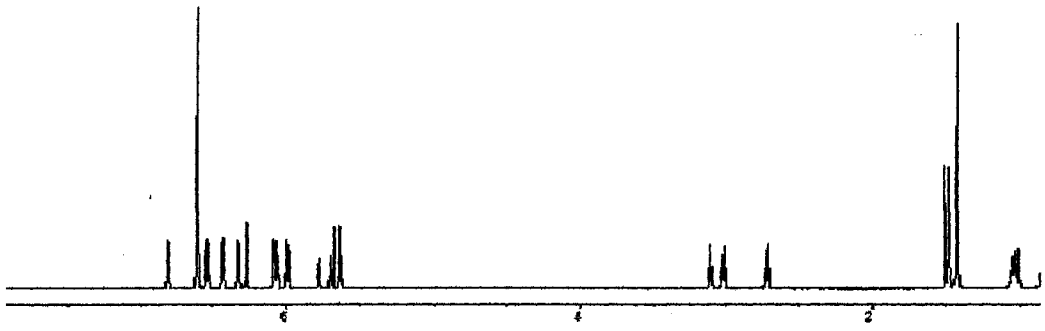


Figure 2.6: ^{1}H NMR spectrum of **(141)** in C_6D_6.

The second "pure" compound to be eluted was concluded to be **(145)** based on the NMR experiments, its IR and mass spectra. Again, the ^{1}H NMR spectrum ($CDCl_3$ solution) provided the most information (Figure 2.7). It exhibited one OCH_2 signal (4H) and one CH_3 signal (12H), which pointed toward relatively high symmetry.

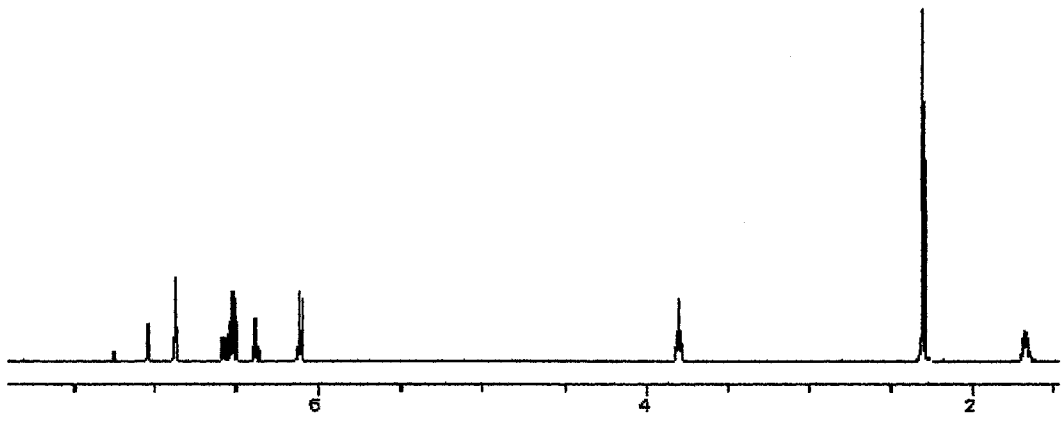
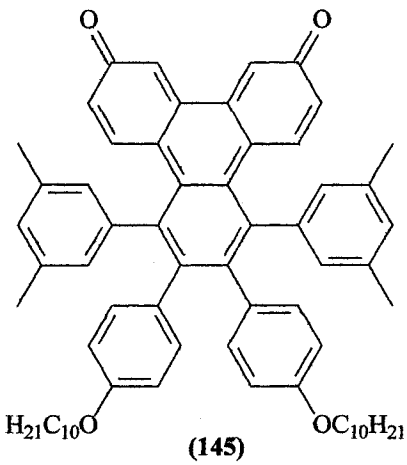


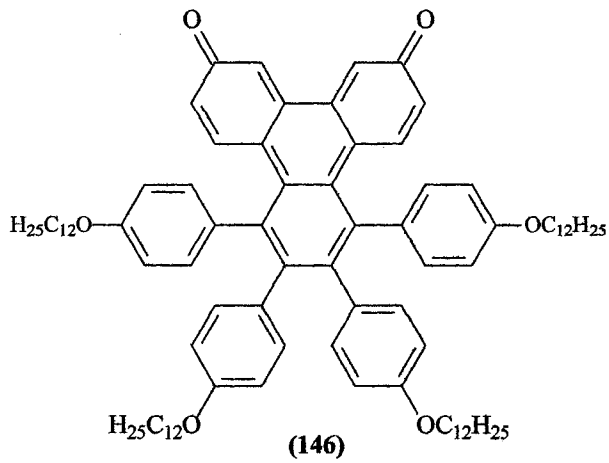
Figure 2.7: ^{1}H NMR spectrum of **(145).**

The integral value of the OCH_2 signal indicated the loss of two decyl groups. the aromatic region contained two relatively broad, weakly coupled (^{1}H, ^{1}H-COSY spectrum) singlets (4H and 2H), which were consistent with two intact 3,5-dimethylphenyl groups. An AA`XX` system (8H) pointed toward two intact and

symmetry related 4-decyloxyphenyl groups. A three spin system (each 2H) consisting of a doublet of doublet, a doublet (J = 6.0 Hz) and a doublet (J = 9.0 Hz) pointed toward cyclodehydrogenation having occurred between two 4-decyloxyphenyl groups. As with the first compound, signals attributable to phenolic OH groups were not observed. Since additional cyclodehydrogenations can be ruled out by the ^{1}H NMR spectrum, quinone formation presented itself as the only plausible explanation. The IR spectrum contains a strong peak at 1666 cm^{-1}, which consistent with the carbonyl stretching frequencies range (1690-1660) of quinones found in the literature.[113] Moreover, the mass spectrum (APCI) contained a strong peak at *m/z* = 931.6 which is totally consistent with the formation of **(145)** (m = 931.3). A similar quinone structure **(146)** was reported by Müllen, and this compound exhibited very similar NMR, IR and UV-Vis data to **(145)**. If **(145)** is the correct structure, it was formed in 74% yield.



(145)



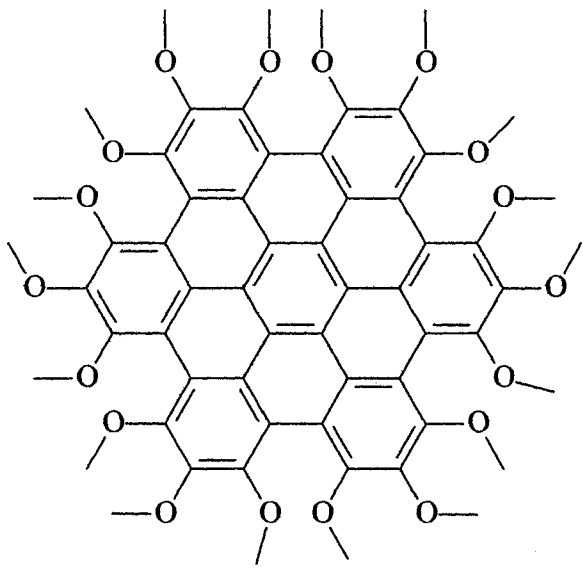
(146)

It is worth mentioning that the generation of an extended quinonoid system incorporating the central aromatic ring is possible via oxidative dealkylation and dehydrogenation.[110] It is also well known that in the presence of Lewis acids

[113] Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*, Prentice-Hall, New Jersey **1998**, 212.

compounds similar to **(145)** can undergo reactions that involve ether cleavage and oxidation to quinoid aromatic structures in addition to the formation of a new C-C bond between the adjacent rings.[114] The occurrence of these competing processes is system dependant.

The problem of partial closure may yet be solved through modification of the reaction conditions and variation of the Lewis acid. The dealkylation problem, which was initially surprising in view of Müllen's successful synthesis of **(147)** using $FeCl_3$,[61] appeared to be a more serious problem. It was therefore decided to forgo further work on the system with decyloxy solublizing groups and switch attention to a system with a different solublizing group.



(147)

The *tert*-butyl group has been used extensively as a solublizing group, even though it is not one of the most effective of solublizing groups. On the other hand, it brings with it synthetic simplicity and it effectively blocks reactions from occurring at the adjacent sites. It has also been used often in HBC synthesis. The new synthetic

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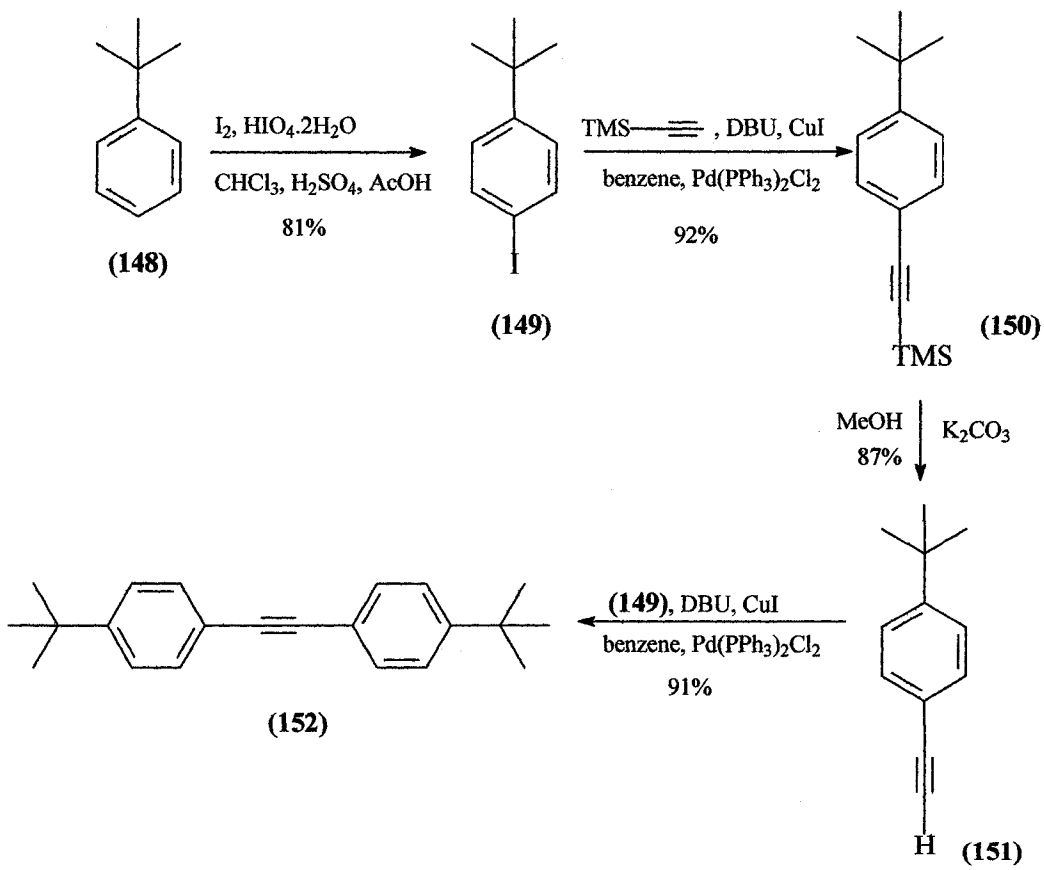
[114] a) Musgrave, O. C. *Chem. Rev.* **1969**, *69*, 499-531-. b) Kovacic, P.; Jones M. B.; *Chem. Rev.* **1987**, *87*, 357-379. c) Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* **1995**, *18*, 191-195.

route, which was analogous to the previous one, was initiated with the iodination of commercially available *tert*-butylbenzene using iodine/periodic acid. Using a modification of a procedure used previously in the Bodwell group,[115] this reaction proceeded successfully to give the iodide **(149)** in 81% yield. The following step was a Sonogashira coupling with TMS-acetylene, which furnished compound **(150)** in 92% yield as an oily brown liquid that upon protiodesilylation furnished **(151)** (87%). Finally, diarylacetylene derivative **(152)** was obtained in 91% yield by Sonogashira coupling of **(151)** and **(149)** (Scheme 2.10).

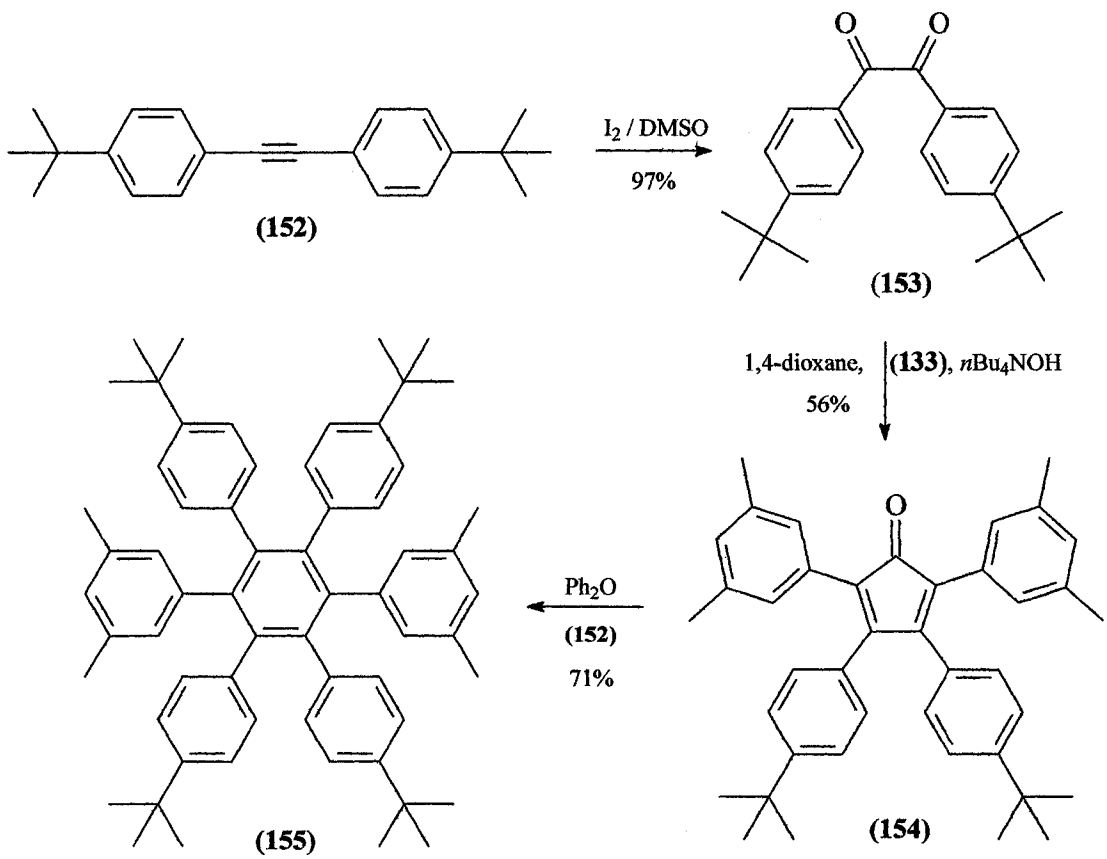


Scheme 2.10: Synthesis of 4,4'-di(*tert*-butylyphenyl)acetylene **(152)**.

[115] Houghton, T. J. *Ph.D. Dissertation*, Memorial University of Newfoundland, **1999**.

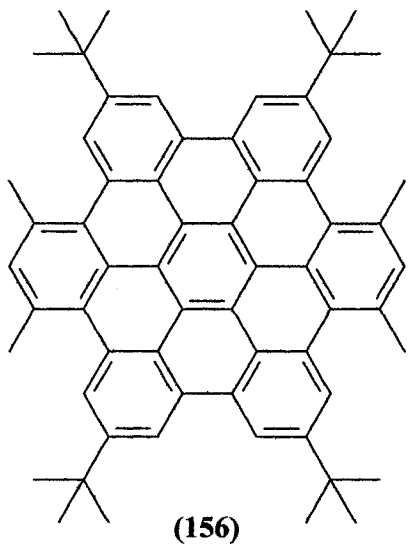
The synthesis proceeded with the oxidation of **(152)** using I_2/DMSO to provide the diketone **(153)** in 97% yield. This was then converted into cyclopentadienone **(154)** by double Knövenagel condensation with diarylacetone **(133)**. The yield for this step (56%) was similar to that obtained for the synthesis of **(140)** (51%).

IEDDA reaction of the cyclopentadienone **(154)** with alkyne **(152)** afforded, following loss of CO the initially formed adduct, hexaarylbenzene derivative **(155)** in 71% yield as a white solid (Scheme 2.11). By comparison, hexaarylbenzene **(141)** was obtained as sticky oil, which better demonstrates the pronounced effect of the long decyloxy group on the physical properties of a system it is attached to.



Scheme 2.11: Synthesis of substituted benzene derivative **(155)**.

It was immediately apparent that that hexaarylbenzene **(155)** was considerably less soluble than **(141)** and this necessitated the development of a different work-up. Whereas crude **(141)** was subjected directly to column chromatography, **(155)** was first slurried three times (3x50 mL) with petroleum ether to remove the diphenylether and then dissolved in dichloromethane. The resulting solution was poured into methanol to precipitate **(155)** as a white powder. Although the yield (71%) and purity of **(155)** obtained by this procedure were both very good, the low solubility at this stage did not bode well for the Scholl reaction leading to the targeted HBC **(156)**.

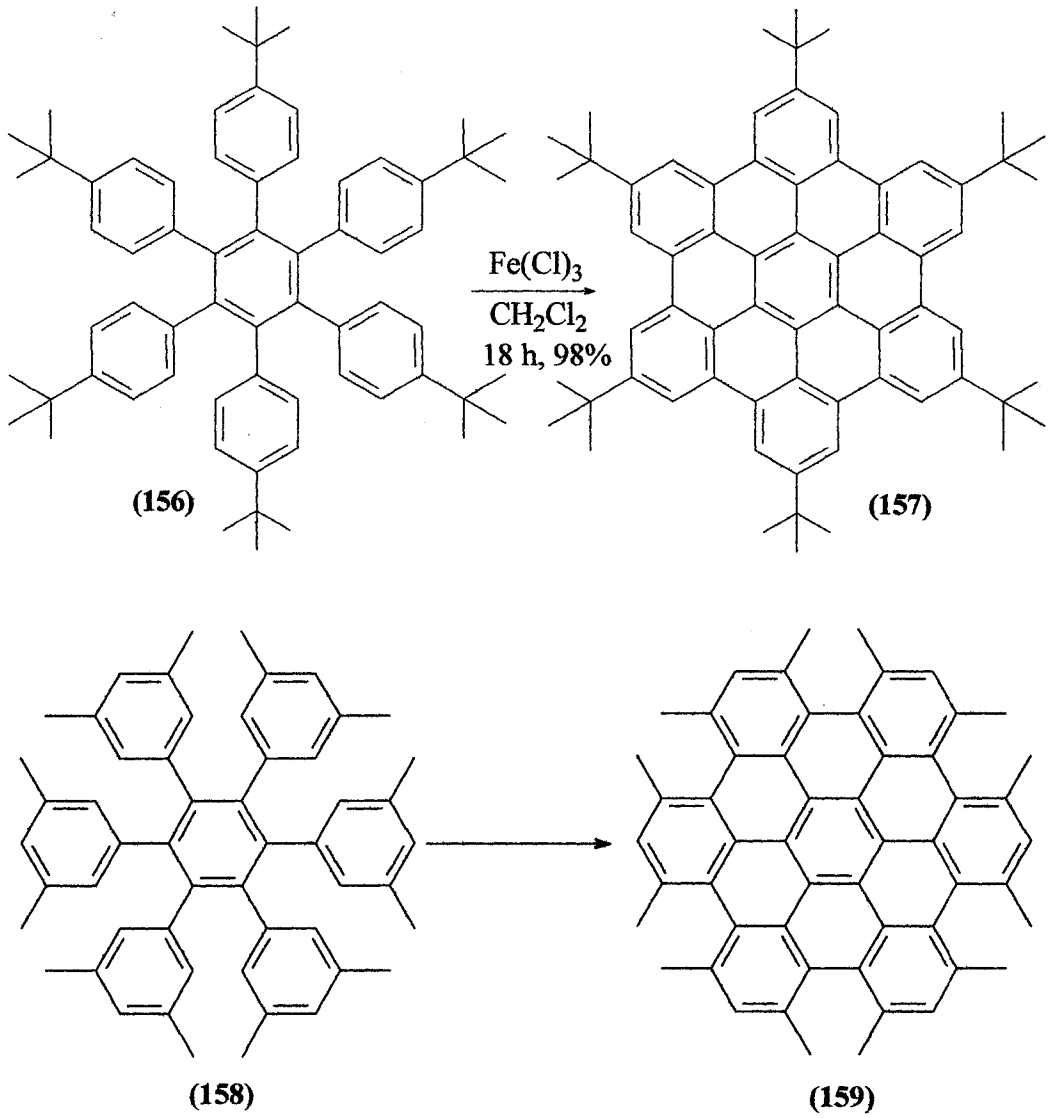


(156)

The first attempt to prepare HBC **(156)** was conducted using the same set of conditions used for the attempted synthesis of **(142)**. Disappointingly, the starting material was not fully consumed, even after prolonged reaction. This was surprising in view of reports that hexaarylbenzenes (157)[116] and **(158)**[117] were produced in

[116] Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 1834-1839.

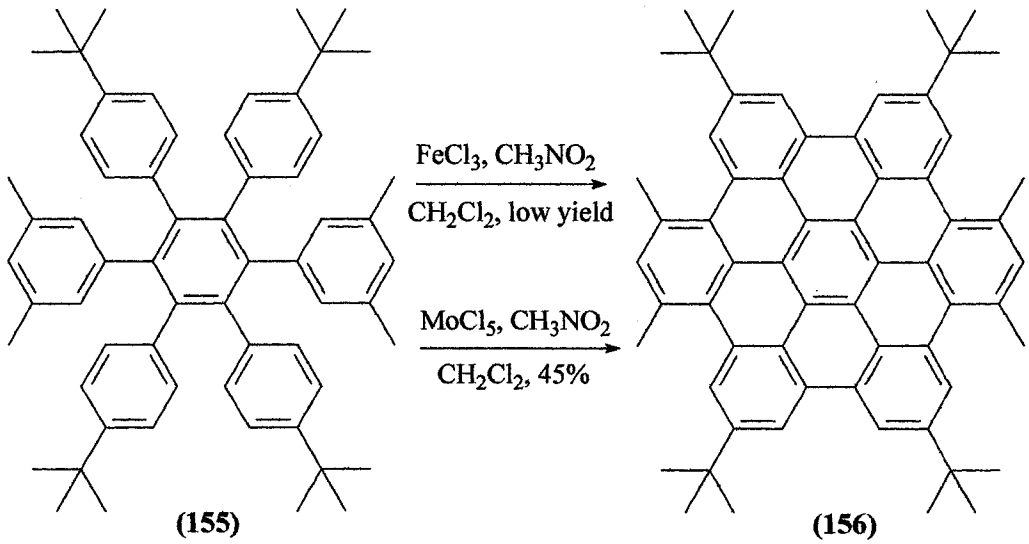
almost quantitative yield established ferric chloride conditions[118] (Scheme 2.12). As feared, the crude product mixture exhibited very low solubility and, despite considerable effort, HBC **(156)** could not be isolated from this mixture in anything approaching pure form. However, TLC and ^{1}H NMR analysis was consistent with the formation of some of the desired product.



Scheme 2.12: Examples of HBCs Using $FeCl_3$ in CH_2Cl_2 synthesized by Müllen.

[117] Watson, M. D.; Fechtenkötter, A. .; Müllen, K.; *Chem., Rev.*; **2001**, *101*, 1267-1300.
[118] a) Koch, N.; Heimel, G.; Wu, J.; Zojer, E.; Johnson, R. L.; Brédas, J-L.; Müllen, K.; Rabe, J. *Chem. Phys. Lett.* 2005, *413*, 390-395. b) Wehmeier, M.; Wagner, M.; Müllen, K. *Chem. Eur. J.* **2001**, *7*, 2197-2205.

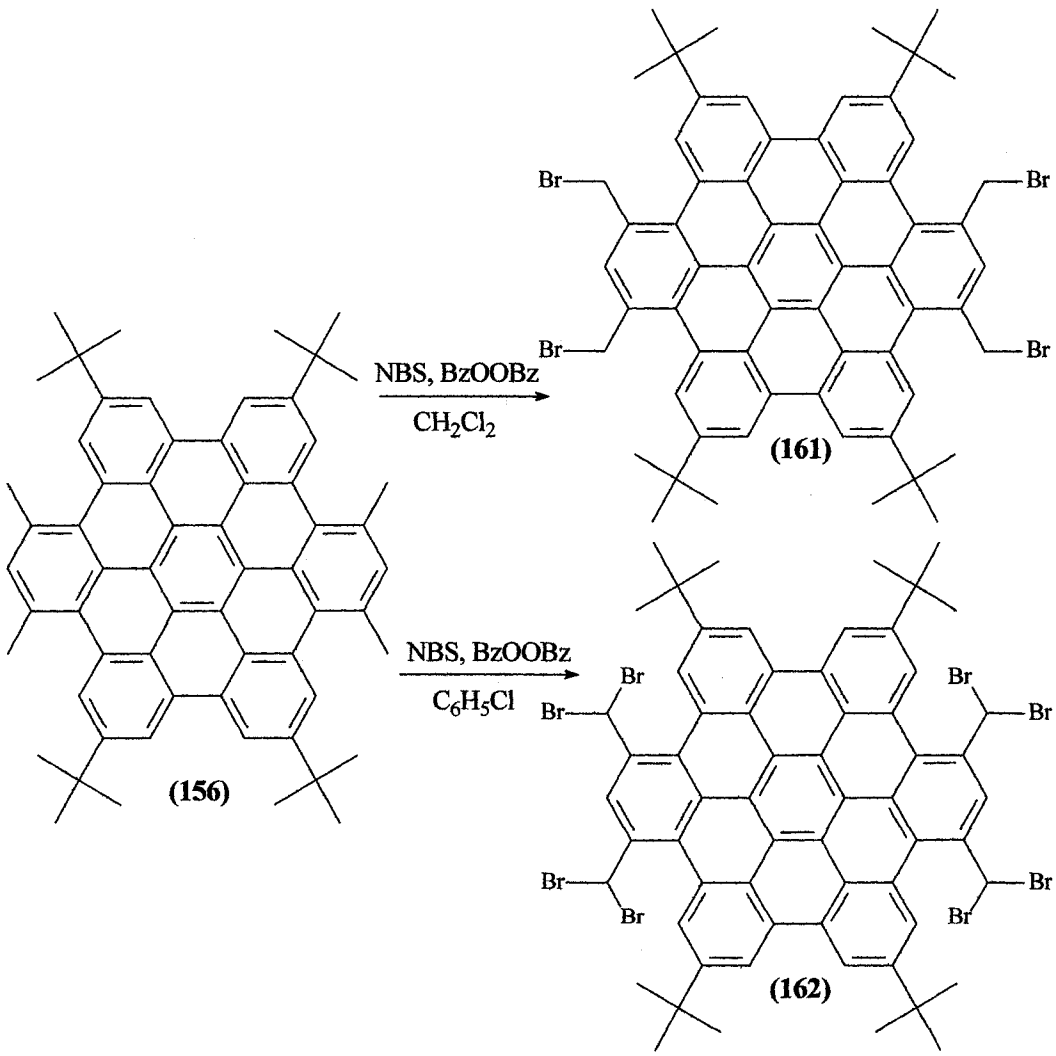
The use of a different Lewis acid catalyst, $MoCl_5$,[70] was then investigated, but the outcome of the reaction was similar to the previous ones with $FeCl_3$. However, upon increasing the number of equivalents of Lewis acid ($MoCl_5$) from 2 to 3 per H atom lost from the substrate, it was found that the starting material was fully consumed after 30 min. According to TLC and ^1H NMR analysis, the crude reaction mixture contained a much higher proportion of HBC **(156)** (*ca.* 90%), but it was still not as pure as desired. The low solubility ruled out chromatographic purification and various attempts to increase purity by washing, recrystallization and precipitation were unsuccessful.



Scheme 2.13: Attempted synthesis of hexabenzocoronene **(156)**.

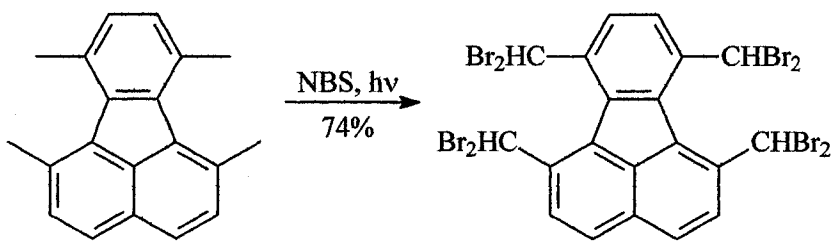
Nevertheless, sufficient quantities of HBC **(156)** were available for initial investigation of its fourfold benzylic bromination. Common solvents for free radical bromination (*e.g.* CCl_4, benzene, CH_2Cl_2) were not able to dissolve sufficient amounts

of HBC **(156)**, so reactions were carried out in chlorobenzene, in which **(156)** showed somewhat better solubility. In general, the first and the second bromination of a CH_3 group under free radical conditions do not have largely different rates. As a consequence, molecules that have more than one methyl group react to give mixtures of products with all combination of zero, one and two bromine atoms on the benzylic carbon atoms. The selective monobromination of the methyl groups of a system with more than one benzylic methyl group is therefore usually a low yielding process, and the situation worsens as the number of methyl groups increases.



Scheme 2.14: Attempted bromination of HBC **(156)**.

An exception to this general situation has been observed for hindered benzylic groups. For example, Siegel[119] reported that NBS bromination of **(163)** to **(164)** proceeded in very good yield (Scheme 2.15). The methyl groups in molecular board **(156)** are hindered, so there was some cause for optimism that selective fourfold monobromination could be achieved. The attempted bromination reactions of **(156)** were monitored by TLC, which indicated the formation of several new products. However, despite varying the number of equivalents of NBS (4.4 equivalents to give **(161)** and 8.8 equivalents to give **(162)**, no one product appeared to accumulate selectively in either experiment. The product mixtures were again difficult to analyze due to low solubility and work on this synthesis was consequently brought to close at this time. Clearly, the *tert*-butyl groups are not effective enough solublizing groups for the purposes of this project. Furthermore, it appears (at least from initial observations) that the process of introducing functionality at this relatively late stage will be nontrivial, and the introduction of functionality at an early stage will have to be investigated anew.



(163) **(164)**

Scheme 2.15: Examples of hindered benzylic brominations reported by Siegel.

[119] Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2000**, *123*, 527-525

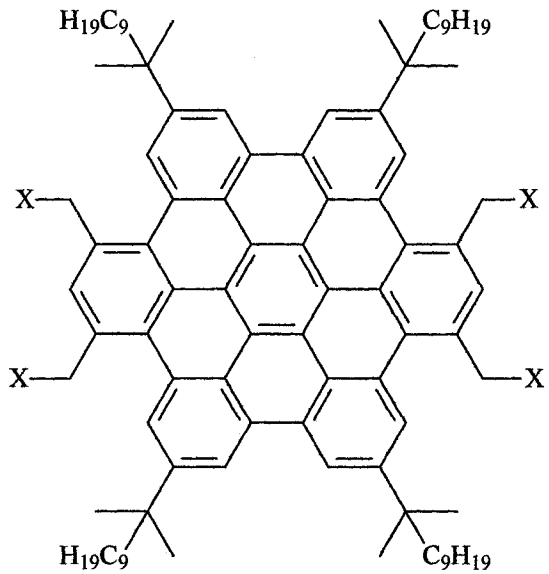
2.5 - Conclusions and future work

The synthesis of an aromatic belt was approached according to a strategy that involves (1) the synthesis of an appropriately substituted molecular board, (2) the union of two such boards to form a tetrathiacyclophane, (3) its conversion to a cyclophanetetraene and (4) application of the VID reaction to give a belt. The use of Müllen's HBC chemistry to achieve the first of these four objectives was the primary focus of this work and, although the goal was not fully met, a board without functionality was prepared and the ground work was laid for the subsequent completion of this part of the plan.

Attempts to convert mesitylene **(121)** or trimesic acid **(122)** into functionalized precursors to appropriately functionalized HBCs were unsuccessful, so work was conducted on unfunctionalized systems with the expectation that functionality could be introduced at later stage. Although this paved the way for progress to be made, preliminary work aimed at introducing the desired functionality after the HBC had been formed was unpromising. Future work will certainly have to include the introduction of functionality at an early stage. In other words, the initial synthetic approach will have to be revisited.

Another key issue that surfaced was the nature of the solublizing groups on the HBC. With decyloxy groups present, solubility, handling and purification were generally not problematic. However, these groups were incompatible with the Scholl reaction. The use of *tert*-butyl solublizing group circumvented the incompatibility with the Scholl reaction, but they were much less effective solublizing groups. Problems associated with solubility emerged as early as the hexaarylbenzene stage. Future work will have to focus on solublizing groups that effectively maintain solubility at and beyond the HBC stage and that also survive the Scholl reaction. For

example, these could be 2-methyl-2-undecyl groups as shown in **(165)**. These groups combine length, have no functionality that may lead to incompatibility problems, and lack benzylic protons, which would be problematic if free radical bromination is to be used to introduce functionality at late stage (where X = H in **(165)**).



(165 X= H)

(166 X= Br)

Once a reliable route to multigram quantities of appropriately substituted, sufficiently soluble molecular boards **(166)** (X=Br) has been developed, work aimed at completing the remaining stages of the strategy can be undertaken.

2.6 - Experimental

General: compounds are reported in the sequence in which they were synthesized and mentioned in the text. Reactions were performed under N_2 unless it was stated otherwise. Solvents used were either reagent grade, distilled or degassed except for diphenylether which was passed through a column of alumina and reserved under nitrogen and having a stream of nitrogen running through it before use. All chemicals

were reagent grade and were used as received. Chromatographic separations were conducted with Merk silica gel 60 (particle size 40-63 μm, 230-400 mesh). Melting points were determined on Fisher Johns apparatus and are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained on Brüker spectrometer. ^{1}H shifts are relative to internal standard; ^{13}C shifts are relative to the solvent resonance ($CDCl_3$: δ= 77.23). NMR spectra from this chapter are shown in Appendix A. Infrared spectra are provided by a Brüker TENSOR 27 infrared spectrometer.

1,3,5-Benzenetricarboxylate (123)

To a solution of trimesic acid **(122)** (50.5 g, 210 mmol) in MeOH (160 mL), of H_2SO_4 (10 mL) was injected and the reaction was left to proceed under reflux for 18 h under N_2 atmosphere. After completion, the reaction mixture was left to cool to room temperature and the solvent was removed under reduced pressure. Recrystallization from xylene gave colorless needles that were vacuum filtered and dried under high vacuum to give triester **(123)** in 91% yields. Mp 143-145 °C (Lit. 144-144.5 °C).[120]

1,3,5-Tris(hydroxymethyl)benzene (124)

Trimethyl-1,3,5-benzene tricarboxylate **(123)** (1.81 g, 7.93 mmol) in THF (25 mL) was added slowly through a needle into a 250-mL flask containing $LiAlH_4$ (1.81 g, 47.6 mmol) in dry THF (75 mL) at 0° C under a N_2 atmosphere . The ice-bath was removed after addition was completed and the mixture was left to stir at room temperature overnight. The reaction was then quenched with a mixture of Celite and $NaHSO_4 \cdot 7H_2O$ and the suspension was filtered then the Celite was washed twice with excess methanol. Following removal of the solvent, the desired product **(124)** was obtained in 95% yields. Mp. 75-77 °C (Lit. 77°C). ^{1}H NMR (500 MHz, CD_3OD) δ:

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[120] a) Dimick, S. M.; Powell, S. C.; McMahon, S. A.; Moothoo, D. N.; Naismith, J. H.; Toone, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 10268-10296. b) Ashton, P. R.; Anderson, D. W.; Brown, C. L.; Shipway, A. N.; Stoddart, J. F.; Tolley, M. S. *Chem. Eur. J.* **1998**, *4*, 781-795.

7.25 (s, 6H,), 4.61 (s, 3H,). The melting point and the ^{1}H NMR of the product matched that of the authentic material.[121]

1-Bromomethyl-3,5-dimethylbenzene (131)

To a 500 mL round bottom flask equipped with a condenser were added (14.8 g, 83.2 mmol) of *N*-bromosuccinimide and CH_2Cl_2 (250 mL)under a stream of N_2. Mesitylene **(121)** (10.0 g, 83.2 mmol) was added to the solution followed by benzyl peroxide (~5 mg). The solution was irradiated with visible light for 4 h at room temperature. The reaction was quenched with water and extracted 3 times with water (200 mL). The organic layer was dried with magnesium sulfate, filtered, and evaporated. The remaining faint yellow oily solid was chromatographed with hexane to give **(131)** (10.1 g, 50.9 mmol) in 61% yields. Mp. 37-40 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.01 (s, 2H,), 6.93 (s, 1H), 4.43 (s, 2H,), 2.30 (s, 6H,). The ^{1}H NMR of the product matched that of the authentic material.[122]

1,3-Bis(3,5-dimethylphenyl)acetone (133)

To a mixture of **(131)** (12.00 g, 60.28 mmol), NaOH (14.8 g, 371 mmol), and benzyltriethylammonium chloride (0.53 g, 2.30 mmol) in dichloromethane (198 mL) and water (9.9 mL), iron pentacarbonyl (5.94 mL, 8.86g, 45.21 mmol) was added. The reaction mixture was refluxed for 20 hours under N_2 atmosphere. The reaction mixture was then poured into 6N HCl solution and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/hexane), (1/3, v/v) to afford **(133)** (2.92 g, 1.10

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[121] a) Cochrane, W. P.; Pauson, P. L.; Stevens, T. S. *J. Chem. Soc. (C)*, **1968**, 630-632. b) Brousmiche, D. W.; Serin, J. M.; Fréchet, J. M. J.; He, G. S.; Lin. T.-C.; Chung, S.-J.; Prasad, P. N.; Ramamurthi, K.; Tan, L.-S. *J. Phys. Chem. B* **2004**, *108*, 8592-8600. c) Diez-Barra, E.; García-Martínez, J., C.; Merino, S.; del Ray, R.; Rodríguez-López, J.; Sánchez-Verdú, P.; Tejeda J. *J. Org. Chem.* **2001**, *66*, 5664-5670.

[122] A) Bastianelli, C.; Caia, V.; Cum, G.; Gallo, R.; Mancini, V.; *J. Chem. Soc., Perkin Trans. 2*, **1991**, *5*, 679-683.B) Ishii, Y.; Kikuchi, D.; Sakaguchi, S.; *J. Org. Chem.*; **1998**, *63*, 6023-6026

mmol) in 37% yield. (Mp. 50-52 °C) (Let. 50 °C).[123] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.91 (s, 2H), 6.77 (s, 2H), 3.64 (s, 4H), 2.30 (s, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 206.58, 138.50, 134.24, 128.96, 127.57, 49.41, 21.43; Ms (EI): *m/z* (%): 266.2 (40) $[M]^+$.

1-decyloxy-4-iodobenzene (135)

to a solution of commercially available 4-iodophenol **(134)** (4.40 g, 20.0 mmol) in anhydrous ethanol (50 mL) in a 250 mL round bottom flask equipped with a condenser were added KOH (1.12 g, 20.0 mmol) and KI (0.07 g, 0.40 mmol) under a N_2 stream. The mixture was heated to 60° C and bromodecane (4.42 g, 20.0 mmol) was added dropwise. The reaction mixture was refluxed overnight then cooled to room temperature. The precipitates were removed by filtration then the solvent was evaporated by reduced pressure to give an oily liquid which after chromatography on silica gel using dichloromethane/hexane (2/1, v/v) as the eluent was isolated (6.74, 18.7 mmol) in 94% yield of **(135)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (AA`XX` half spectrum, 2H) 6.83 (AA`XX` half spectrum, 2H), 3.96 (t, 2H), 1.81-1.76 (m, 2H), 1.48-1.42 (m, 2H), 1.37-1.29 (m, 12H), 0.89 (t, 3H). The ^{1}H NMR of the product matched that of the authentic material.[122]

1-Decyloxy-4-(trimethylsilylethynyl)benzene (136)

To a stirred mixture of 1-decyloxy-4-iodobenzene **(135)** (7.00 g, 19.4 mmol), (trimethylsilyl)acetylene (2.80 g, 28.5 mmol), CuI (0.29 g, 1.52 mmoles) and dichloro-bis(triphenylphosphine) palladium (II) (0.27 g, 0.38 mmol) in benzene (45 mL) at 0°C and under N_2 stream, DBU, (4.34 g, 29.2 mmol) was added. The ice-bath was removed after addition was completed and the reaction mixture was left to stir for 20 h at room temperature. After evaporation of solvent, the product was isolated by

[123] Thépot, J. Y.; Lapinte, C. *J. Organometallic Chem.* **2001**, *627*, 179-188.

column chromatography on silica gel using dichloromethane/hexane (1/9, v/v) as the eluent; yield **(136)** (6.41g, 19.4 mmol 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (AA`XX` half spectrum, 2H) 6.81 (AA`XX` half spectrum, 2H), 3.95 (t, 2H), 1.81-1.76 (m, 2H), 1.48-1.42 (m, 2H), 1.37-1.29 (m, 12H), 0.89 (t, 9H), 0.24 (s, 3H). The ^{1}H NMR of the product matched that of the authentic material.[124]

1-Decyloxy-4-ethynelbenzene (137)

To a solution of 1-decyloxy-4-(trimethylsilylethynyl)benzene, **(136)** (5.26g, 15.9 mmol) in methanol (100 mL), K_2CO_3 (2.86 g, 20.7 mmol) was added and the reaction mixture was stirred for 6 h at room temperature. The reaction mixture was then poured into cold water and extracted with dichloromethane. After washing with brine solution, the organic layer was dried with magnesium sulfate and filtered followed by concentration under reduced pressure. The resulting liquid was chromatographed using dichloromethane/hexane (1/4, v/v) to give **(137)** (4.06 g, 15.7 mmol) in 99% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (AA`XX` half spectrum, 2H) 6.84 (AA`XX` half spectrum, 2H), 3.96 (t, 2H), 3.00 (s, 1H), 1.81-1.76 (m, 2H), 1.48-1.42 (m, 2H), 1.37-1.29 (m, 12H), 0.89 (t, 3H). ^{1}H NMR of the product matched that of the authentic material. [125]

4,4'-Di(decyloxyphenyl)acetylene (138)

To a solution of 1-decyloxy-4-iodobenzene **(135)** (5.56 g, 15.4 mmol) , 1-decyloxy-4-ethynelbenzene **(137)** (3.99 g, 15.44 mmol), CuI (289 mg, 1.52 mmol) and dichloro-bis(triphenylphosphine) palladium (II) (0.218 g, 0.311 mmol) in benzene (45 mL) at 0 °C and under N_2 stream, DBU (3.53 g, 23.2 mmol) were added. The ice-bath was removed after addition was completed and the reaction mixture was left to stir for 20 h at room temperature. After evaporation of solvent, the remaining residue was

[124] Lee, S. J.; Park, C. R.; Chang, J. Y. *Langmuir* **2004**, *20*, 9513-9519.

dissolved in dichloromethane and poured into NH_4Cl aq. Solution. After extraction, the organic layer was washed with brine solution and dried with magnesium sulfate which was removed with suction filtration. Removal of the solvent resulted a yellow solid that upon Recrystallization from toluene gave the desired product **(138)** (6.37g, 13.0 mmol) in 84% yields. Mp. 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (AA`XX` half spectrum, 4H) 6.84 (AA`XX` half spectrum, 4H), 3.94 (t, 4H), 1.80-1.74 (m, 4H), 1.47-1.41 (m, 4H), 1.35-1.27 (m, 24H), 0.88 (t, 6H). The ^{1}H NMR matched one from literature.[125]

1,2-Bis(4-decyloxyphenyl)ethane-1,2-dione (139)

A solution of 4,4'-di(decyloxyphenyl)acetylene **(138)** (0.64 g, 1.30 mmol) and iodine (0.20 g, 0.79 mmol) in DMSO (15 mL) was heated at reflux for 20 h under nitrogen atmosphere. The reaction mixture was poured in Na_2SO_3 solution and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography, (dichloromethane/hexane) 30% by volume, to give **(139)** (0.66 g, 1.26 mmol) in 97% yields as a white solid. Mp. 69-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, 4H, J = 9.0 Hz), 6.96 (d, 4H, J = 9.0 Hz), 4.04 (t, 4H), 1.84-1.78 (m, 4H), 1.49-1.43 (m, 24H), 0.89 (t, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.7, 164.7, 132.6, 126.3, 114.9, 68.7, 32.1, 29.7, 29.53, 29.52, 29.2, 26.2, 22.9, 14.32.

2,5-(3,5-Dimethylphenyl)-3,4-(4,4'-decyloxyphenyl)cyclopentadienone (140)

To a refluxing solution of 4,4'-diphenyl diketone **(137)** (0.63 g, 1.21 mmol) and 1,3-bis(3,5-dimethyl)acetone **(133)** (0.32 g, 1.21 mmol) in 1,4-dioxane (0.61 mL), a tetrabutylammonium hydroxide solution (1.0 M, 0.61 mL, 0.61 mmol) in methanol was added. The resulting mixture was heated at reflux for 2 h under a nitrogen

[125] Pugh, C.; Percec, V. *J. Polym. Sci. Part A: Polym Chem. Ed.* **1990**, *28*, 1101-1126.

atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography, (dichloromethane/hexane) 25% by volume, to afford **(140)** (0.45 g, 0.61 mmol) in 51% yield as a dark residual oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.86 (s, 4H,) 6.85(d, 4H, J = 7.5 Hz), 6.70 (d, 4H, J = 8.5 Hz), 3.93 (t, 4H), 2.21(s, 12H), 1.78 (m, 4H), 1.46-1.427 (m, 24H), 0.90 (t, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.0, 159.5, 154.0, 137.4, 131.3, 129.1, 128.1, 125.6, 125.0, 114.0, 68.2, 32.1, 29.8, 29.7, 29.5, 29.4, 26.3, 23.0, 21.6, 14.3; elemental analysis calcd. (%) for $C_{53}H_{68}O_3$ (753.07): C 84.52, H 9.10; found C 84.31, H 9.59.

1,4-Bis(3,5-dimethylphenylbenzene)-2,3,5,6-titrakis(decyloxyphenyl)benzene (141)

A mixture of 4,4'-Bis(decyloxyphenyl)acetylene **(138)** (0.42 g, 0.86 mmol) and **(140)** (0.64 g, 0.86 mmol) in diphenyl ether (5 mL) was heated at reflux for 18 h under nitrogen atmosphere. The hot reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography, (dichloromethane/hexane) 20% by volume, to afford **(141)** (0.35 g, 0.29 mmol) in 81% yield as a brown residual oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.68 (d, 4H, J = 8.5 Hz), 6.43 (s, 2H), 6.40 (d, 4H, J = 8.5 Hz), 6.38 (s, 4H), 3.76 (t, 8H), 1.95 (s, 12H), 1.68-1.63 (m, 8H), 1.40-1.20 (m, 56H), 0.89 (t, 12H); elemental analysis calcd. (%) for $C_{86}H_{118}O_4$ (1215.80): C 84.95, H 9.78; found C 84.81, H 10.20.

Quinone (145)

To a stirring solution of hexaarylbenzene (0.35 g, 0.29 mmol) in CH_2Cl_2 (100 mL) with a continuous stream of N_2 bubbling through it to remove the HCl forming in situ, a solution of $FeCl_3$ (0.90 g, 5.52 mmol) in nitromethane (13 mL) was added dropwise and the reaction mixture was left to stir at room temperature. After 30 min, methanol was added (100 mL) was added and a solid started accumulating which was collected by suction filtration and purified by column chromatography (petroleum ether/ CH_2Cl_2) (1-4) (v/v) furnishing **(145)** as a beige solid in 74% yield (0.20 g, 0.21 mmol). Mp. 291-293 °C. H NMR (500 MHz, $CDCl_3$) δ: 7.267(s, 2H), 6.88 (s, 4H), 6.59 (d, 1H, J = 9), 6.59 (d, 1H, J = 9), 6.53 (d, 4H, J = 12), 6.52 (d, 2H, J = 6), 6.39 (d, 2H, J = 9), 6.11 (d, 4H, J = 9.5) ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.0, 159.3, 150.3, 144.4, 141.7, 138.4, 137.7, 136.0, 135.4, 134.1, 128.8, 127.7, 124.7, 115.4, 110.2, 68.5, 56.8, 32.1, 30.0, 29.7, 29.52, 29.5, 26.13, 22.9, 21.4, 14.3. MS (APCI): *m/z* (%): 931.6 [M^+] (calc. for $C_{66}H_{74}O_4$ = 931.25); IR (neat, ZnSe): ν_{max} [cm^{-1}] = 1666[$(CO)_{stretch}$]; UV/Vis (CH_2Cl_2): λ[nm] (lgε [L mol^{-1} cm^{-1}]): 232(2.36), 331(1.64), 348(1.70).

1-*tert*-Butyl-4-iodobenzene (149)

To a refluxing mixture of I_2 (10.5 g, 41.4 mmol) and $HIO_4.2H_2O$ (2.36 g, 10.3 mmol) stirring in H_2SO_4 (0.73 mL), H_2O (3.64 mL), HOAC (20.6 mL), $CHCl_3$ (25 mL) under N_2, *tert*-butyl benzene **(148)** (6.94 g, 51.7 mmol) was added then the reaction was left to resume overnight. The reaction was quenched with Na_2SO_4 aq. Followed by extraction with petroleum ether. The organic layer was washed with H_2O (3x100 mL), dried with $MgSO_4$ then concentrated under reduced pressure and dried under high vacuum. The resulting yellow liquid was purified by column chromatography, (petroleum ether) to give a colorless liquid **(149)** (10.9 g, 41.9 mmol) in 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (AA`XX` half spectrum, 2H), 7.13 (AA`XX` half spectrum, 2H), 1.28 (s, 9H). The ^{1}H NMR of the product matched that of the authentic material.[126]

1- *tert*-Butyl-4-(trimethylsilylethynyl)benzene (150)

To a stirring mixture of 1-*tert*-butyl-4-iodobenzene **(149)** ((5.11 g, 19.6 mmol), trimethylsilylacetylene (1.93 g, 19.6 mmol), CuI (0.19 g, 0.98 mmoles) and dichloro-bis(triphenylphosphine) palladium (II) (0.34 g, 0.49 mmol) in benzene (45 mL) at 0 °C and under N_2 stream, DBU (4.49 g, 29.5 mmol) was added. The ice-bath was removed after addition was completed and the reaction mixture was left to stir for 20 h at room temperature. After evaporation of solvent, the remaining residue was washed with petroleum ether and poured into NH_4Cl aq. After extraction, the organic layer washed with H_2O (2x100 mL), dried with $MgSO_4$ then concentrated under reduced pressure and dried under high vacuum to give an orange liquid. The product was isolated by column chromatography on silica gel using petroleum as the eluent; yield **(150)** (4.18 g, 18.1 mmol) in 92% yield as a yellow liquid. . ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38 (d, 2H, J = 9.0 Hz), 7.30 (d, 2H, J = 8.5 Hz), 1.29 (s, 9H). The ^{1}H NMR of the product matched that of the authentic material.[127]

1- *tert*-Butyl-4-ethynylbenzene (151)

To a solution of 1-decyloxy-4-(trimethylsilylethynyl)benzene, **(150)** (4.18g, 18.1 mmol) in methanol (30 mL), K_2CO_3 (3.76 g , 27.2 mmol) was added and the reaction mixture was stirred for 6 h at room temperature. The reaction mixture was then poured into cold water and extracted with dichloromethane. After washing with brine solution, the organic layer was dried with magnesium sulfate, concentration under

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[126] A) Ranganathan, S.; Ranganathan, D.; Sigh, S. K. *Tetrahedron. Lett.* **1985**, *26*, 4955-4956. B) Barluenga, J.; Campos, P. J.; .; González, J. M.; Asensio, G. *J. Chem. Soc. Perkin Trans. 1* **1984**, 2623-2624.

[127] Leznoff, C.; Suchozak, B. *Can. J. Chem.* **2001**, *79*, 878-887.

reduced pressure and dried under high vacuum. The resulting liquid was chromatographed using petroleum ether to give **(151)** (2.51 g, 15.9 mmol) in 87% yield as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (d, 2H, J = 8.1 Hz), 7.32 (d, 2H, J = 8.1 Hz), 1.30 (s, 9H). The ^{1}H NMR of the product matched that of the authentic material.[126]

4,4'-Di(*tert*-butylphenyl)acetylene (152)

To a solution of 1-*tert*-butyl-4-iodobenzene **(149)** (3.25 g, 12.5 mmol) , 1- *tert*-butyl - 4-ethynylbenzene **(151)** (1.98 g, 12.5 mmol), CuI (0.024 g, 0.13 mmoles) and dichloro-bis(triphenylphosphine) palladium (II) (0.18 g, 0.25mmol) in benzene (45 mL) at 0 °C and under N_2 stream, DBU, (2.86 g, 18.8 mmol) were added. The ice-bath was removed after addition was completed and the reaction mixture was left to stir for 20 h at room temperature. After evaporation of solvent, the remaining residue was dissolved in dichloromethane and poured into NH_4Cl aq. Solution. After extraction with dichloromethane, the organic layer was washed with brine solution and dried with magnesium sulfate. The solvent was removed in vacuum and the residue was recrystallized from EtOAc/Petroleum ether to give **(152)** (3.30, 11.4 mmol) in 91% yield. Mp. 176-178 °C. H NMR (500 MHz, $CDCl_3$) δ: 7.47 (AA`XX` half spectrum, 4H), 7.37 (AA`XX` half spectrum, 4H), 1.34 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.6, 131.5, 125.6, 120, 89.1, 35.0, 31.4. Both ^{1}H NMR and ^{13}C NMR of the product matched literature values.[114]

1,2-Bis(4-*tert*-butylphenyl)ethane-1,2-dione (153)

A solution of 4,4'-di(*tert*-butylphenyl)acetylene **(152)** (2.00 g, 6.89 mmol) and iodine (1.10 g, 4.20 mmol) in DMSO (40 mL) was heated at reflux for 20 h under nitrogen atmosphere. The reaction mixture was poured in Na_2SO_3 solution and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium

sulfate and concentrated under reduced pressure. The residue was purified by column chromatography, (dichloromethane/petroleum ether) (1/4, v/v) to give **(153)** (2.10 g, 1.26 mmol) in 97% yield as a pale yellow solid which was recrystallized from hexane to give yellow crystals. Mp. 102-104 °C. H NMR (500 MHz, $CDCl_3$) δ: 7.94 (AA`XX` half spectrum, 4H), 7.55 (AA`XX` half spectrum, 4H), 1.37 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 159.1, 130.8, 130.1, 126.2, 35.6, 31.2. Both ^1H NMR and ^{13}C NMR of the product matched literature values.[128]

2,5-(3,5-Dimethylphenyl)-3,4-(4,4'- *tert*-butylphenyl)cyclopentadienone (154)

To a refluxing solution of 4,4'-di(*tert*-butylphenyl) diketone **(153)** (1.31 g, 4.06 mmol) and 1,3-Bis(3,5-dimethyl)acetone **(133)** (1.08g, 4.06 mmol) in 1,4-dioxane (5 mL), a tetrabutylammonium hydroxide solution in methanol (1.0 M, 2 mL, 2.03 mmol) was added. The resulting mixture was heated at reflux for 3 h under a nitrogen atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography, (dichloromethane/hexane) 20% by volume, to afford **(154)** (1.18 g, 2.26 mmol) in 56% yield as a purple solid. Mp. (221-223 °C); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.17 (d, 4H, J = 9.0 Hz,), 6.86 (d, 4H, J = 8.0 Hz), 6.83 (s, 2H), 6.82 (s, 4H), 2.17 (s, 12H), 1.27 (s, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 201.1, 154.7, 151.8, 137.3, 129.3, 129.1, 128.2, 125.36, 124.8, 34.9, 31.44, 21.5; MS (EI): *m/z* (%): 552.3 (74) $[M]^+$.

1,4-Bis(3,5-dimethylphenyl)-2,3,5,6-titrakis(*tert*-butylphenyl)benzene (155)

A mixture of 4,4'-di(*tert*-butylphenyl)acetylene, **(152)** (0.63 g, 2.17 mmol) and **(153)** (1.13 g, 2.17 mmol) in diphenyl ether (5 mL) was heated at reflux for 18 h under

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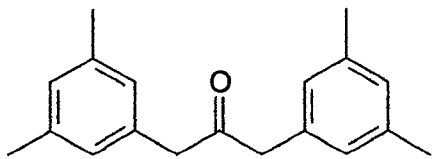
[128] Han, G. Y.; Han, P. F.; Perkins, J.; McBay, H. C. *J. Org. Chem.* **1981**, *46*, 4695-4700.

nitrogen atmosphere. The hot reaction mixture was left to cool to room temperature then access petroleum was added. The forming off-white product was collected by suction filtration and filtered through a short plug of silica, (dichloromethane), to afford a white solid which was dissolved in CH_2Cl_2 and poured into stirring methanol then recollected via suction filtration and vacuum dried to furnish **(155)** (1.25 g, 0.29 mmol) in 71% yields. Mp. >300°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.83 (d, 8H, J = 8.5 Hz,), 6.67 (d, 8H, J = 8.0 Hz), 6.42 (s, 2H), 6.35 (s, 4H), 1.88(s, 12H), 1.24 (s, 36H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.4, 140.5, 140.2, 138.6, 135.4, 131.5, 130.2, 126.4, 123.2, 34.3, 31.4, 21.1.

2,5,11,14-Tetra-*tert*-butyl-7,9,16.18-tetra-methylhexabenzocoronen, (156)

To a stirring solution of hexaarylbenzene **(155)** (0.20 g, 0.25 mmol) in CH_2Cl_2 with N_2 bubbling though it, a solution of $MoCl_5$ (1.34 g, 8.83 mmol) in CH_3NO_2 (16 mL) was added dropwise. The reaction was left to stir at room temperature for 30 min then MeOH (10 mL) was added and the forming precipitate was collected by suction filtration and chromatographed with 5% toluene in hexane to furnish **(156)** as a faint yellow solid (0.088 g, 0.11 mmol) in 45 % yield. Mp. >300°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.27 (s, 4H), 8.97 (s, 4H), 7.82 (s, 2H), 3.34 (s, 12H), 1.77 (s, 36H). ^{13}C NMR not recorded due to the very low solubility of the product.



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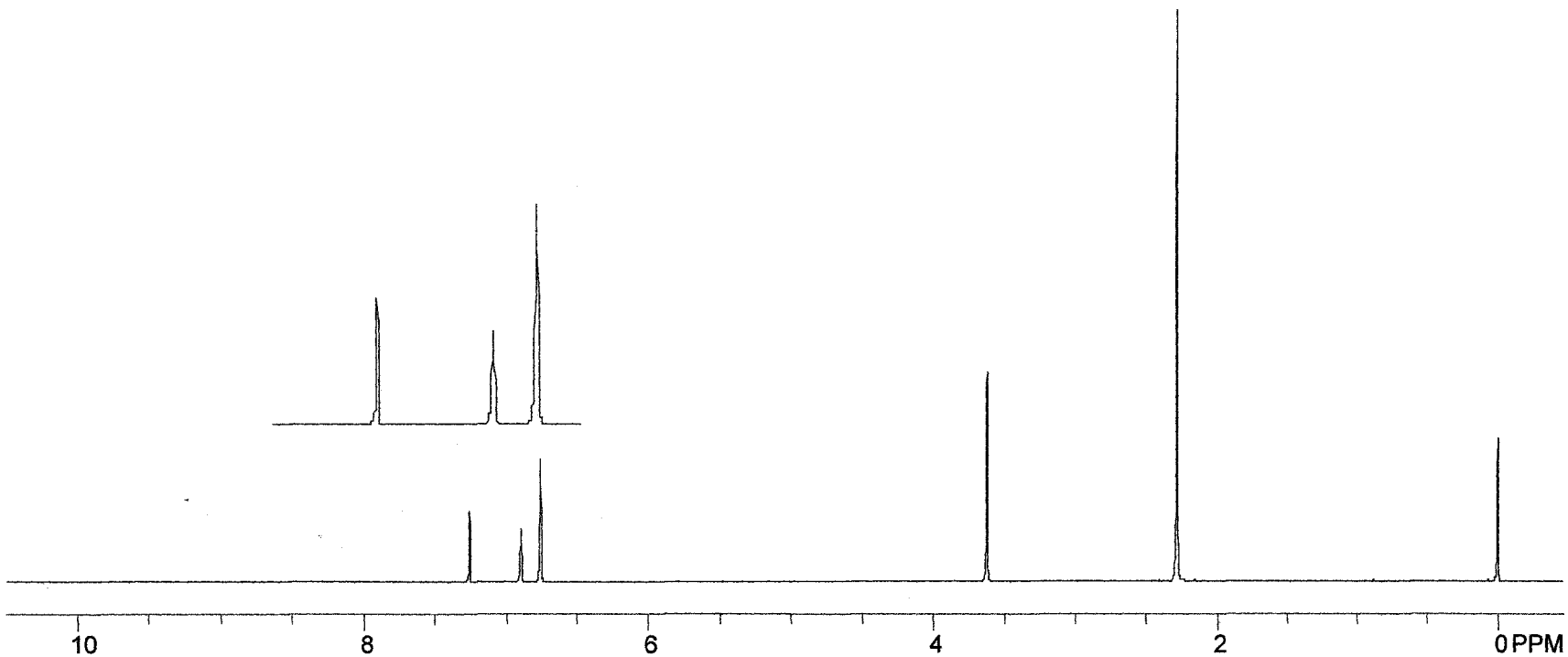

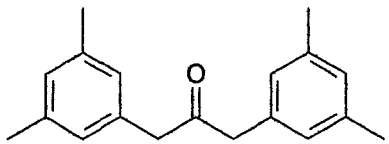

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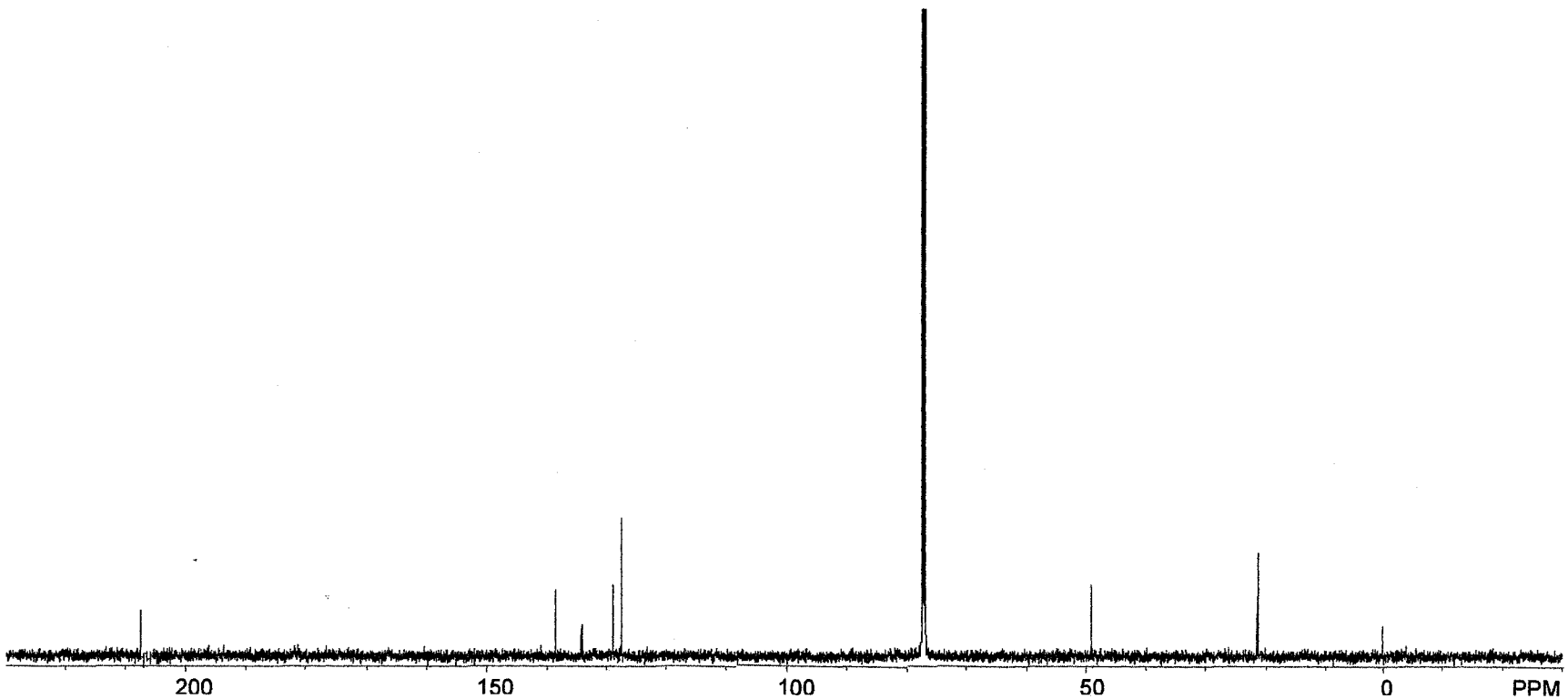

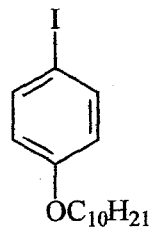

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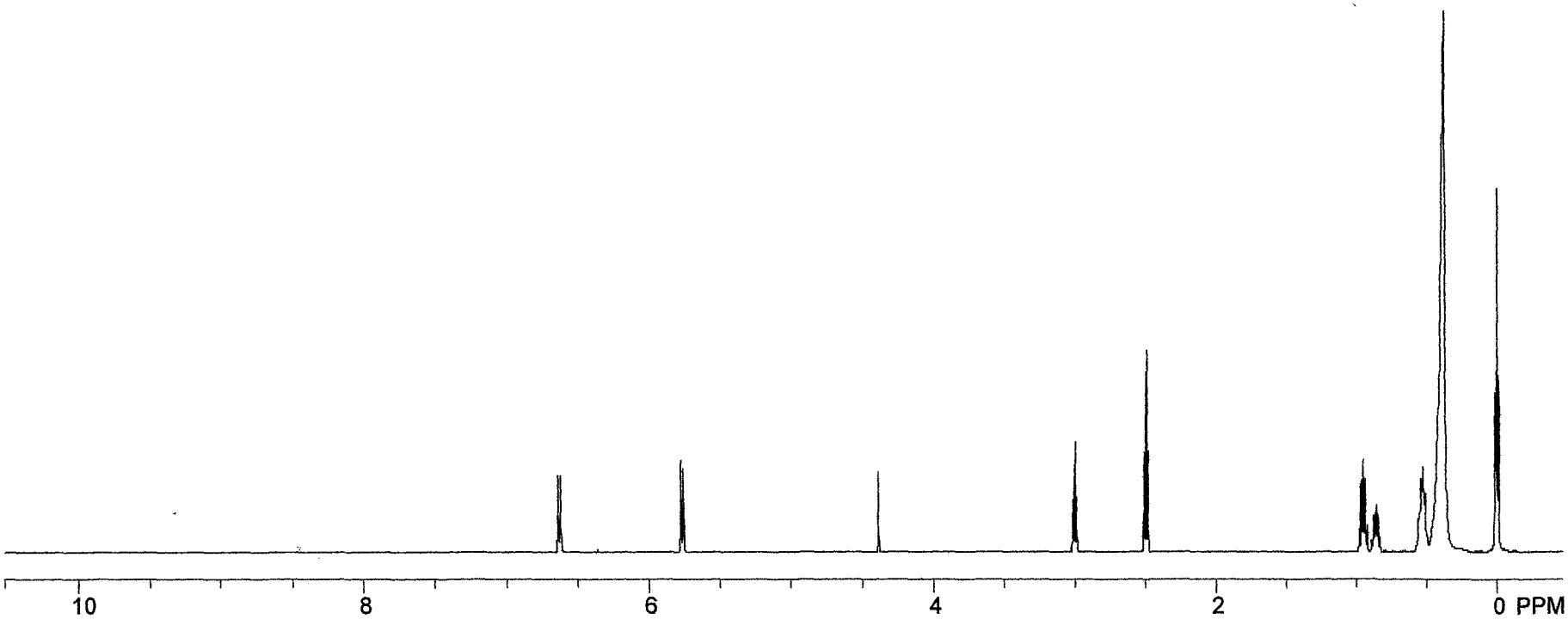

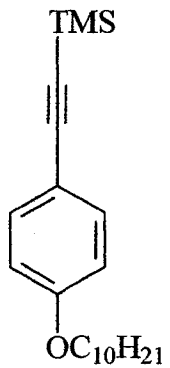

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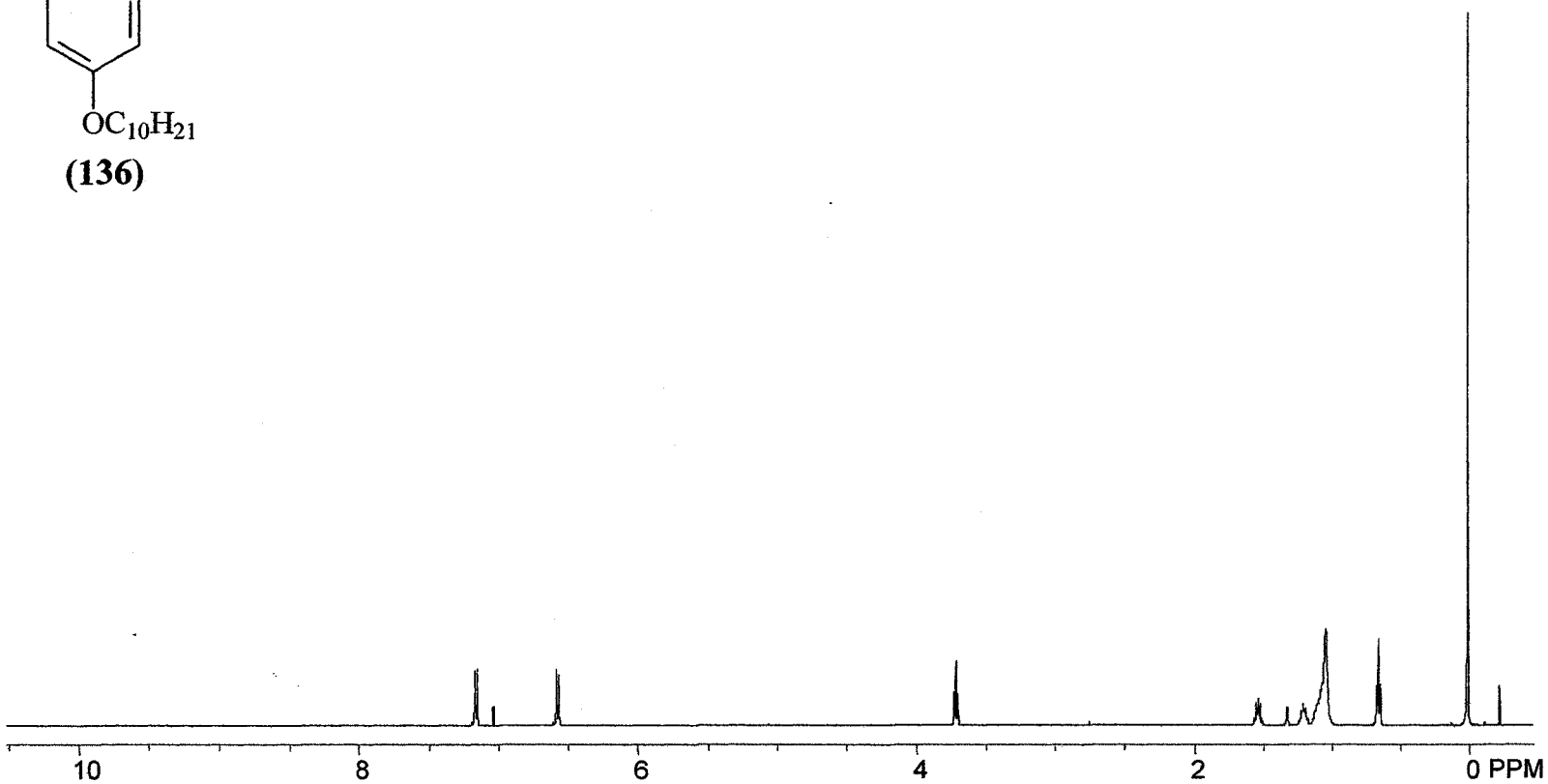

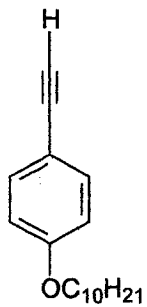

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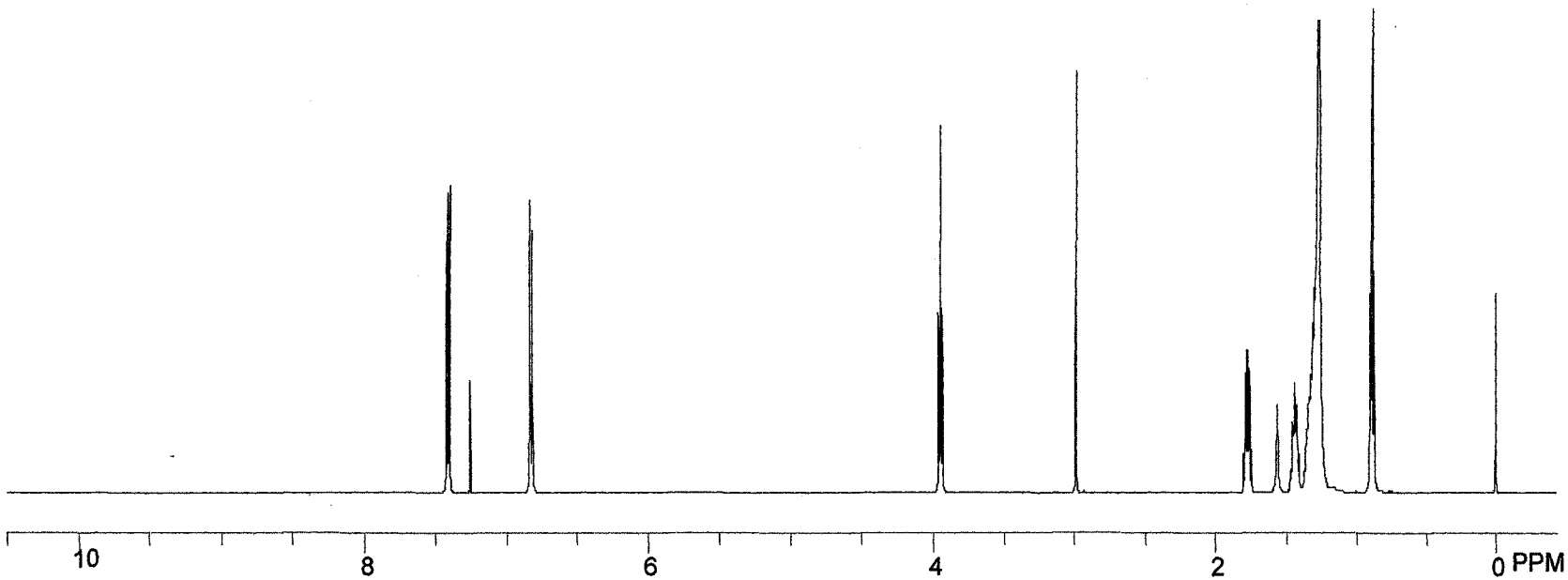

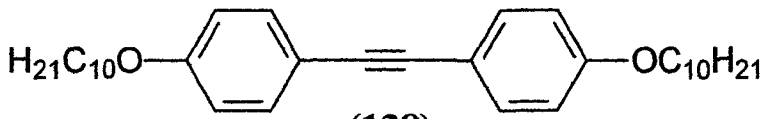

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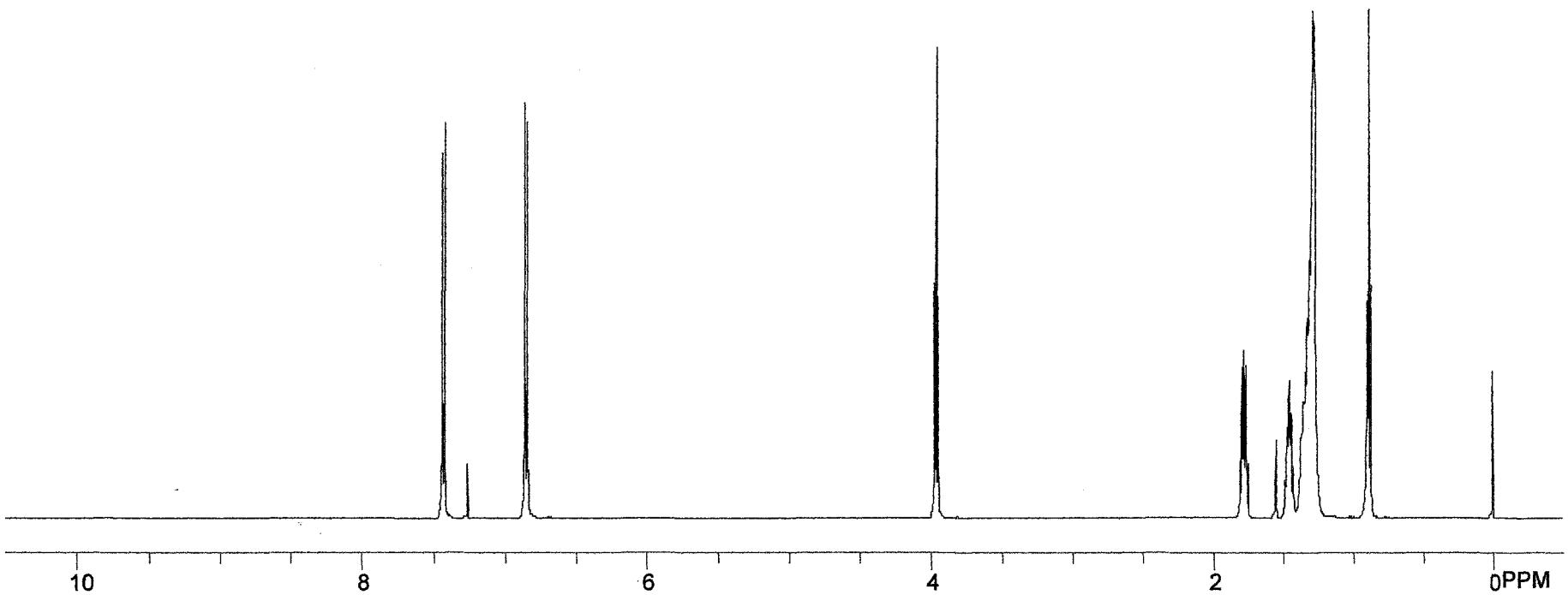

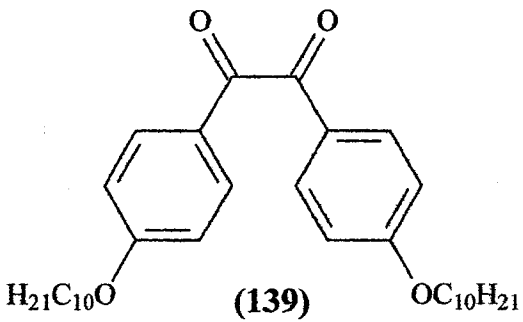

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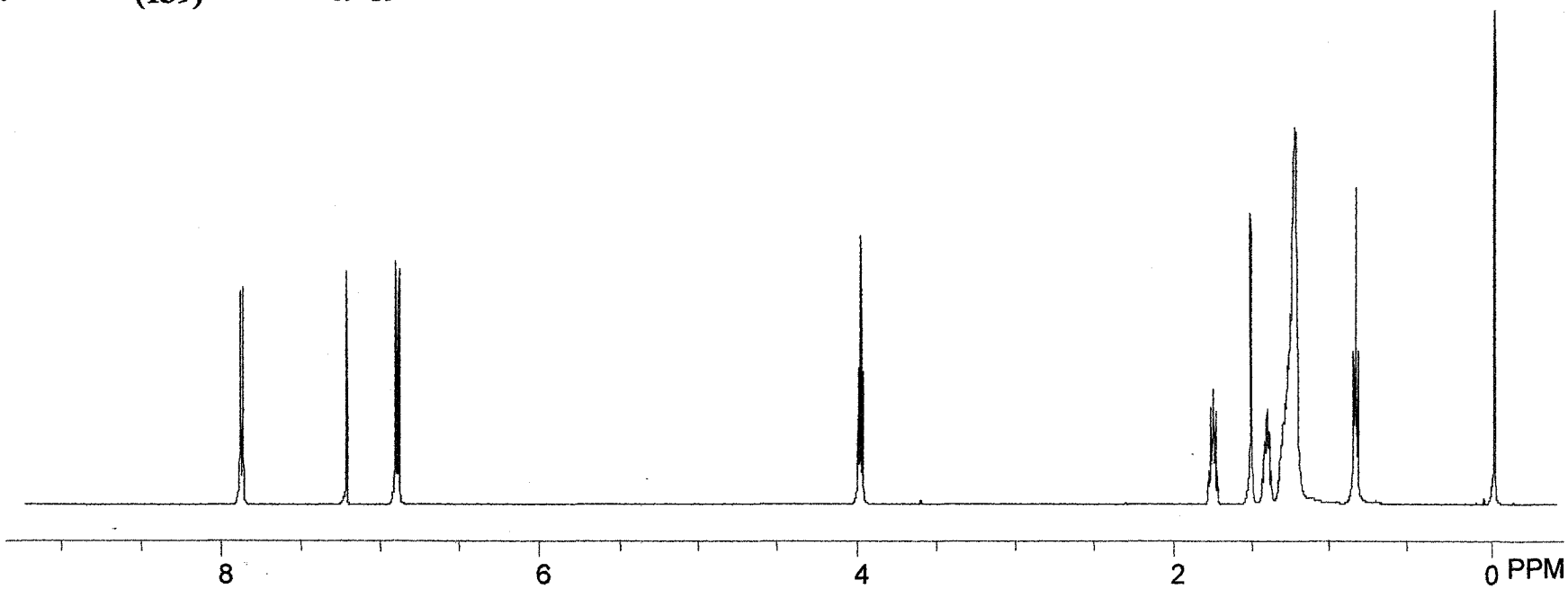

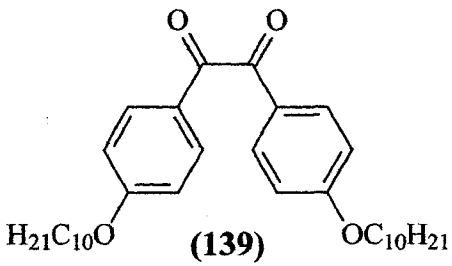

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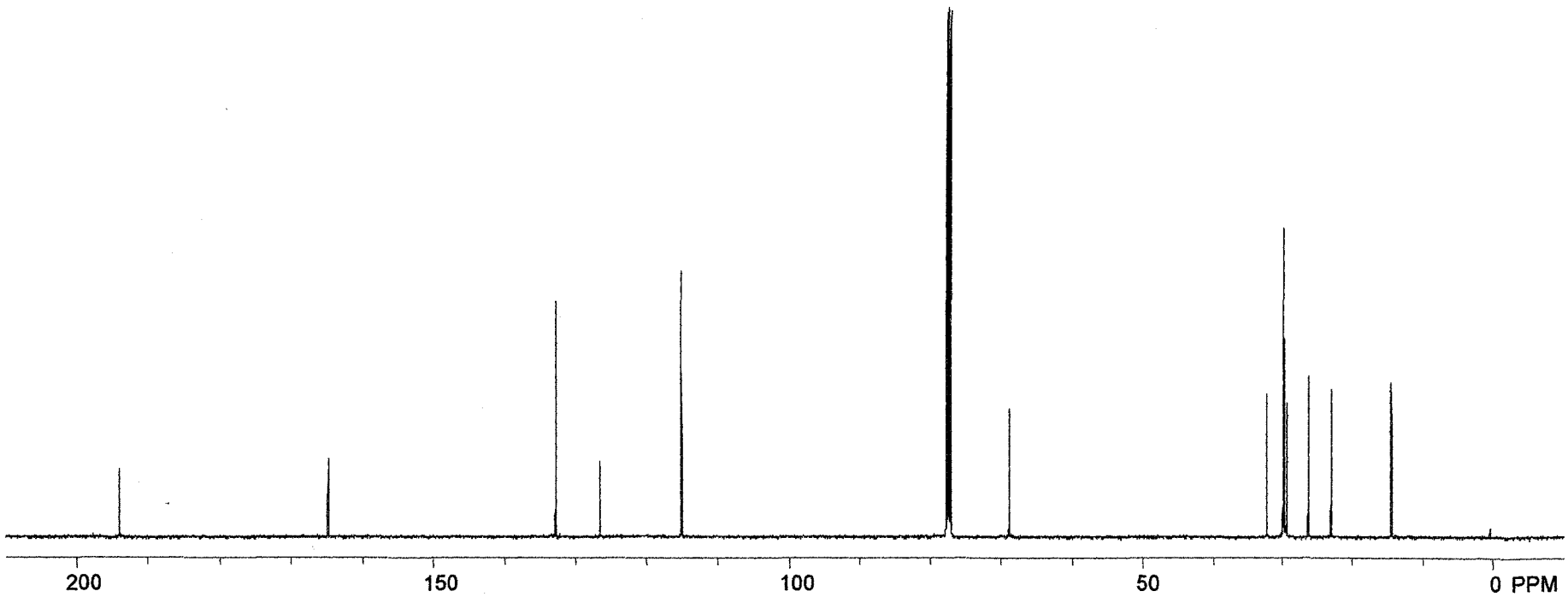

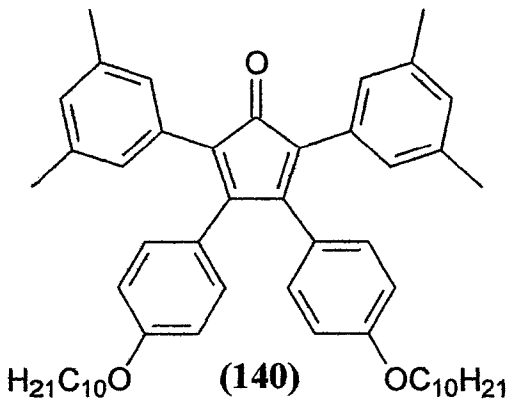

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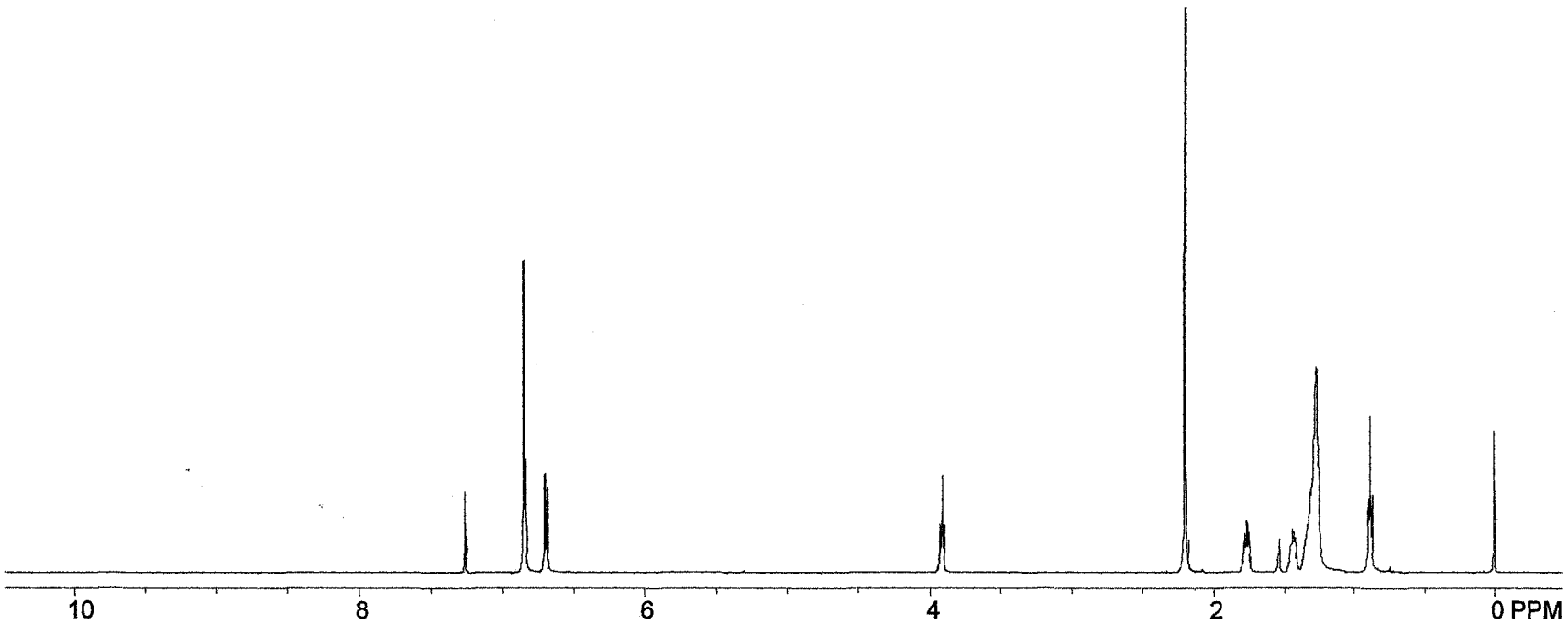

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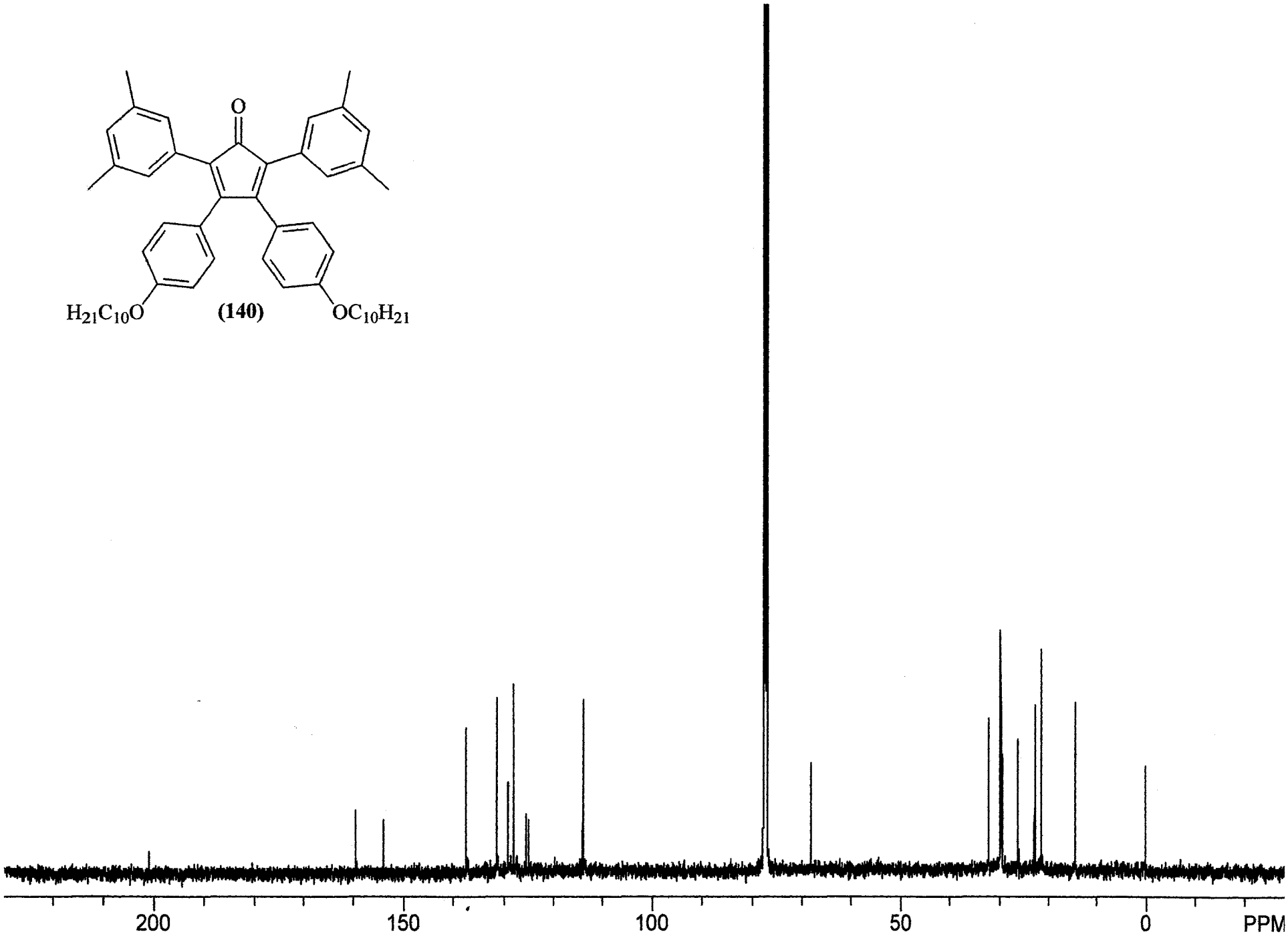

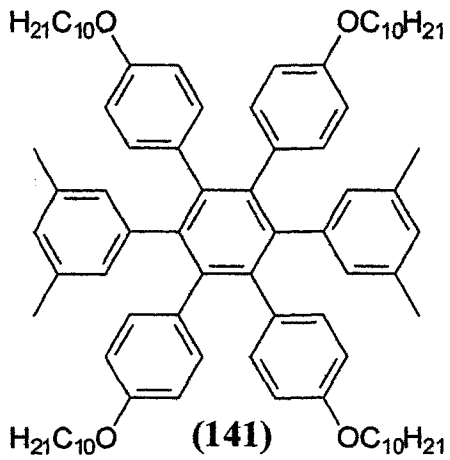

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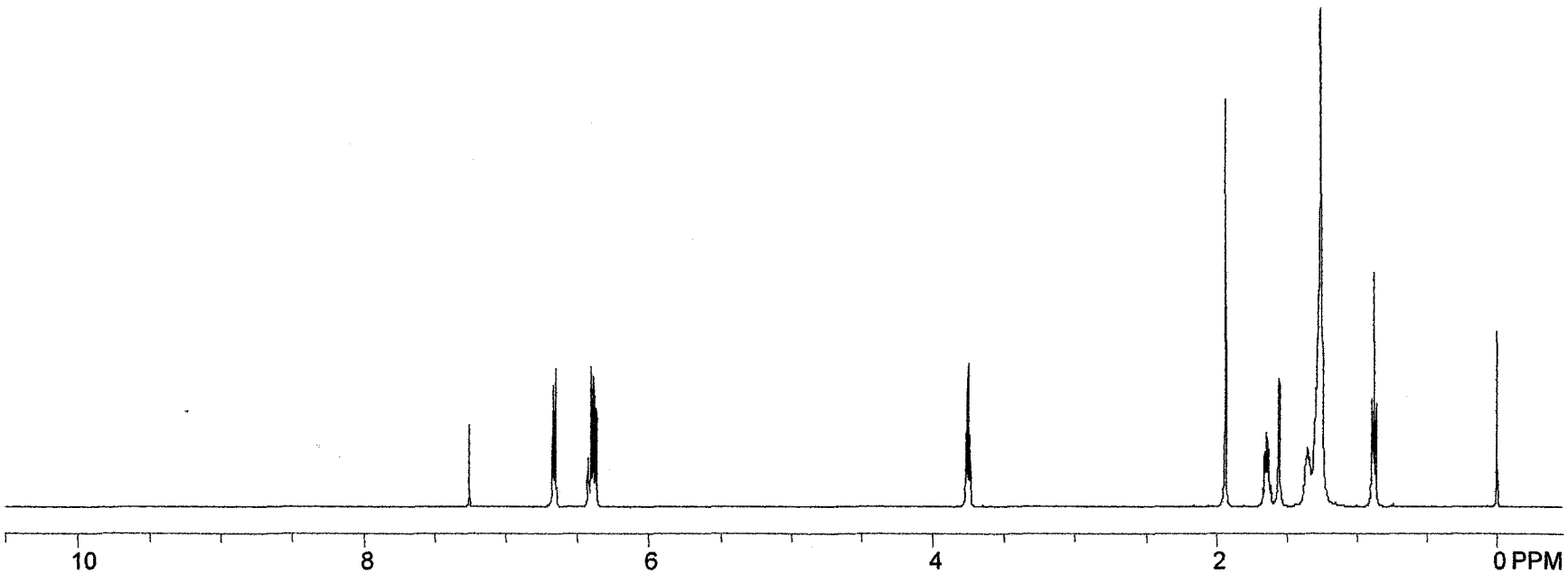

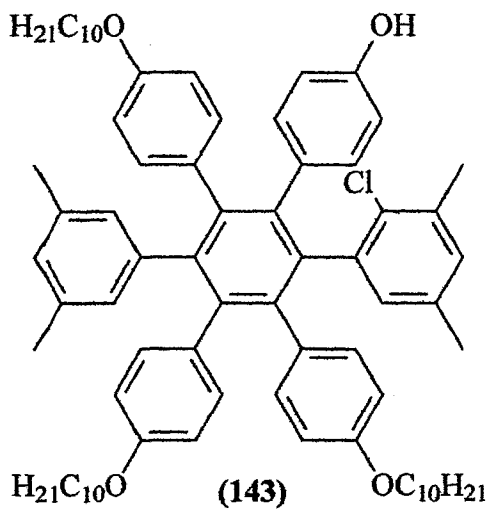

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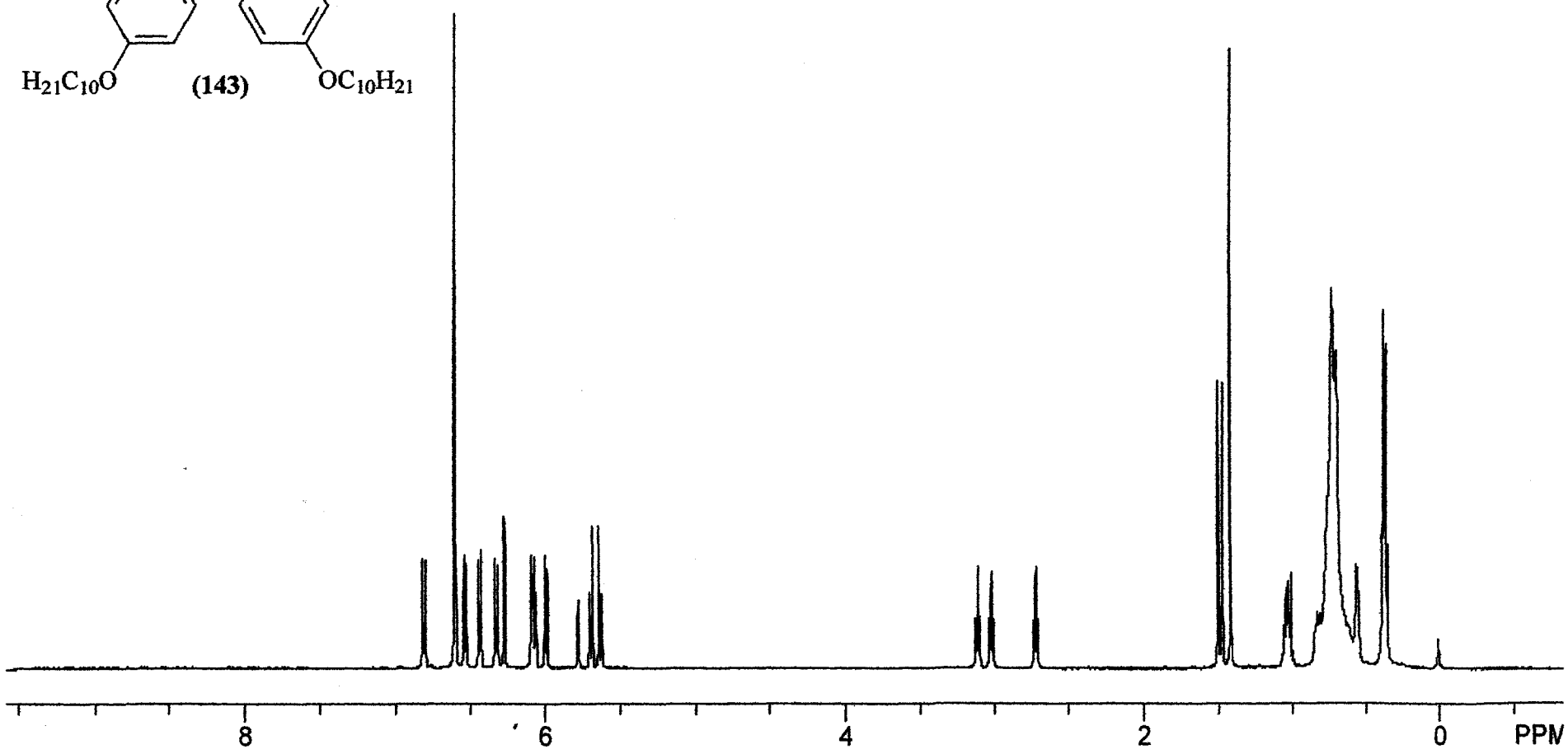

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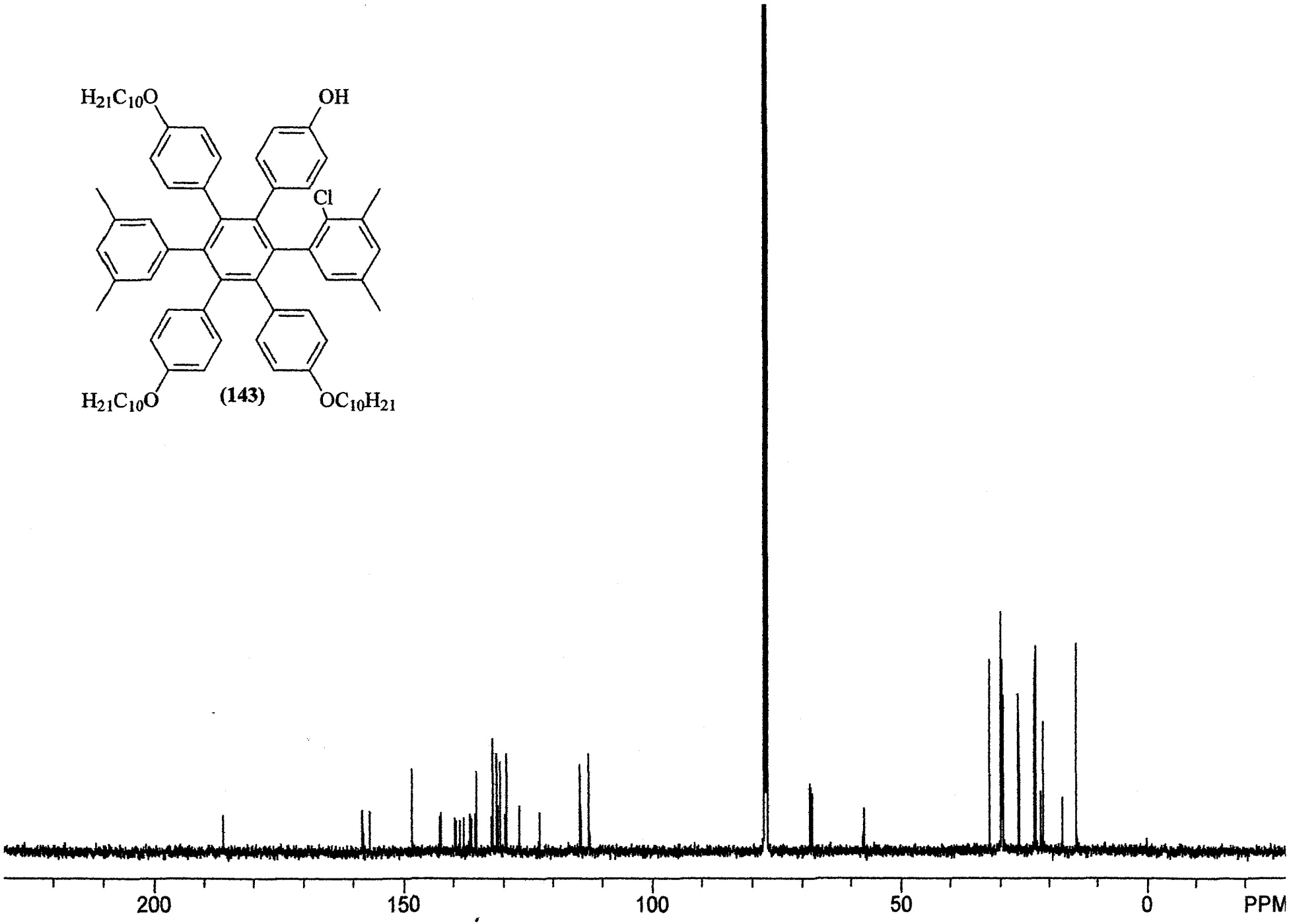

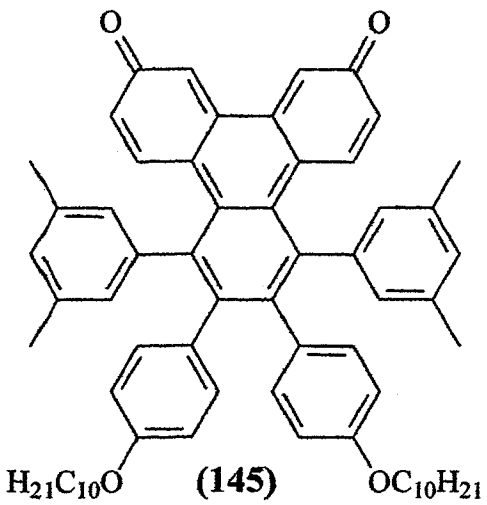

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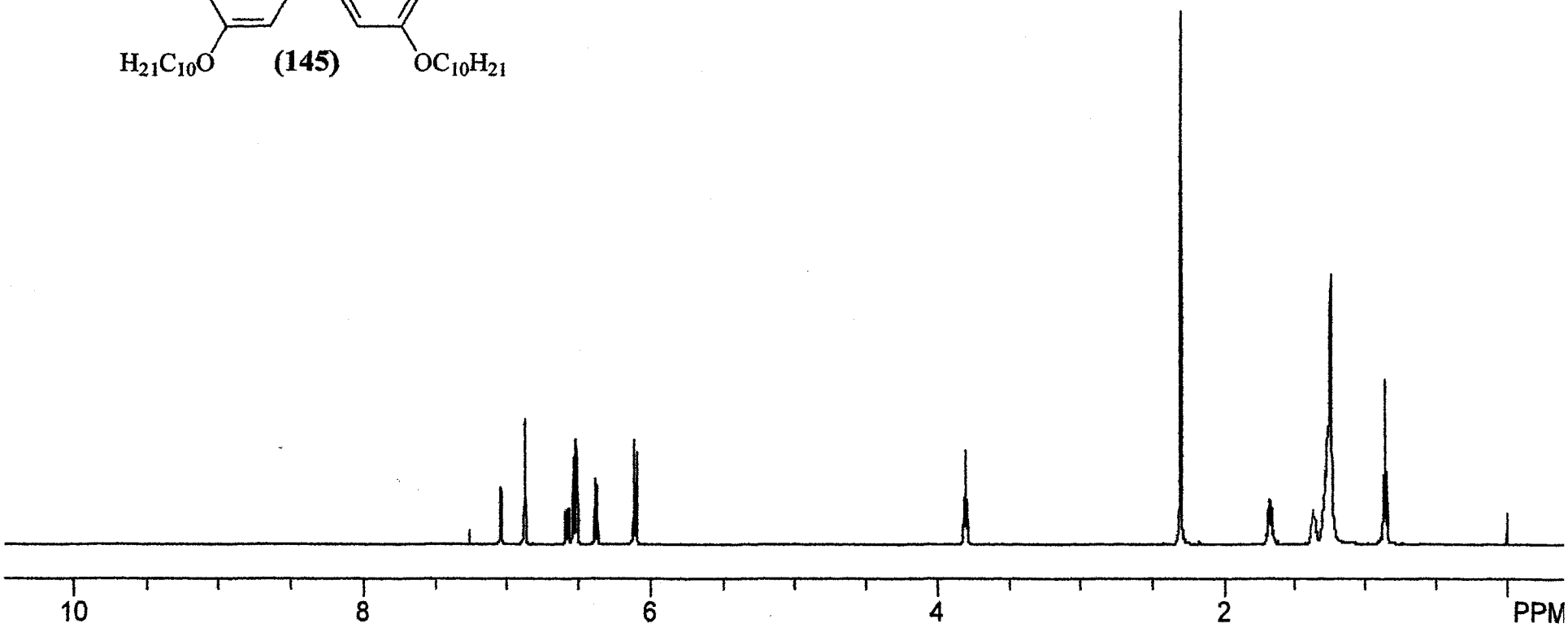

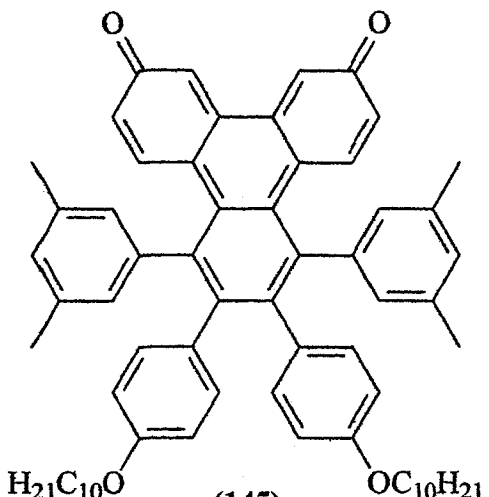

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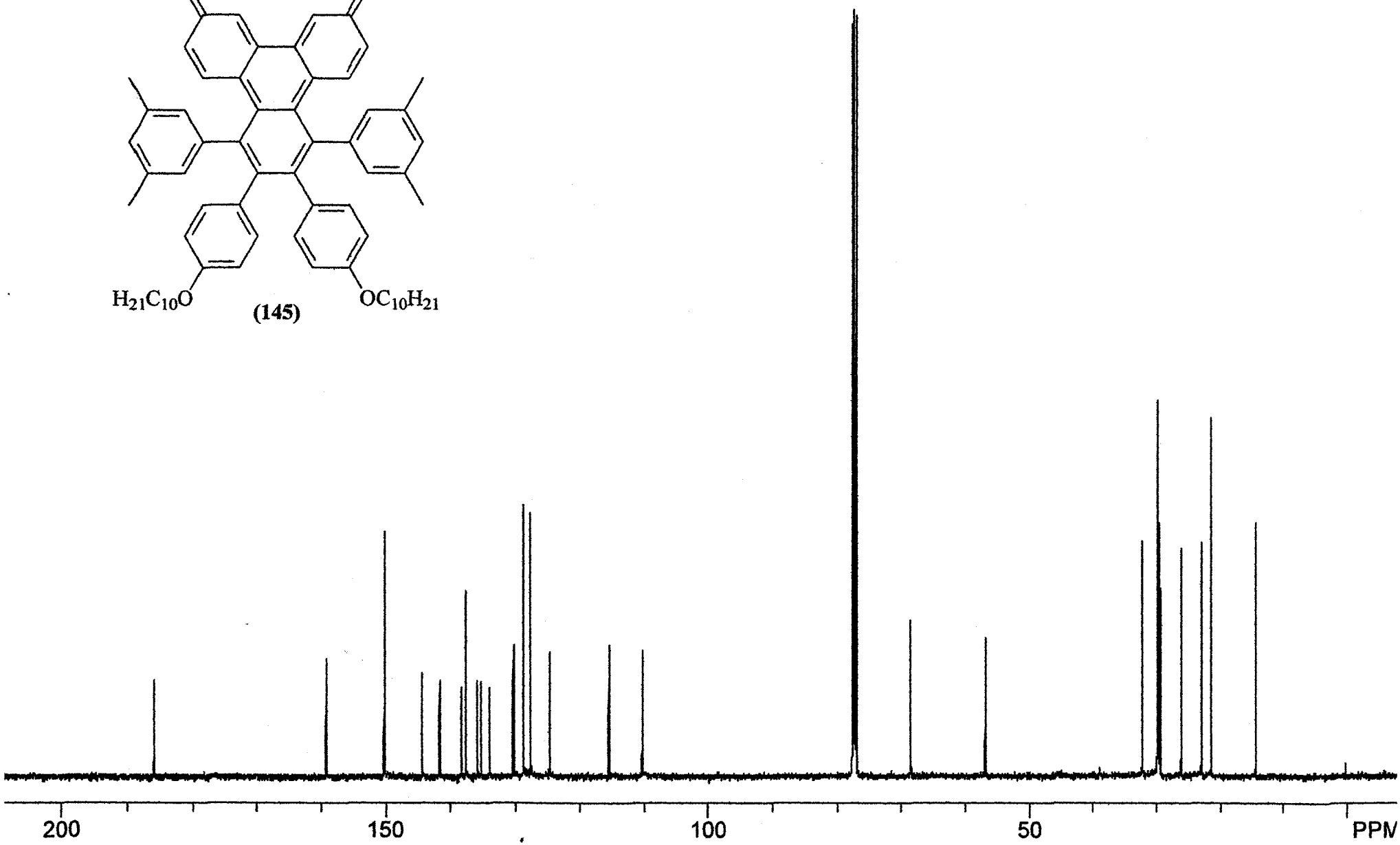

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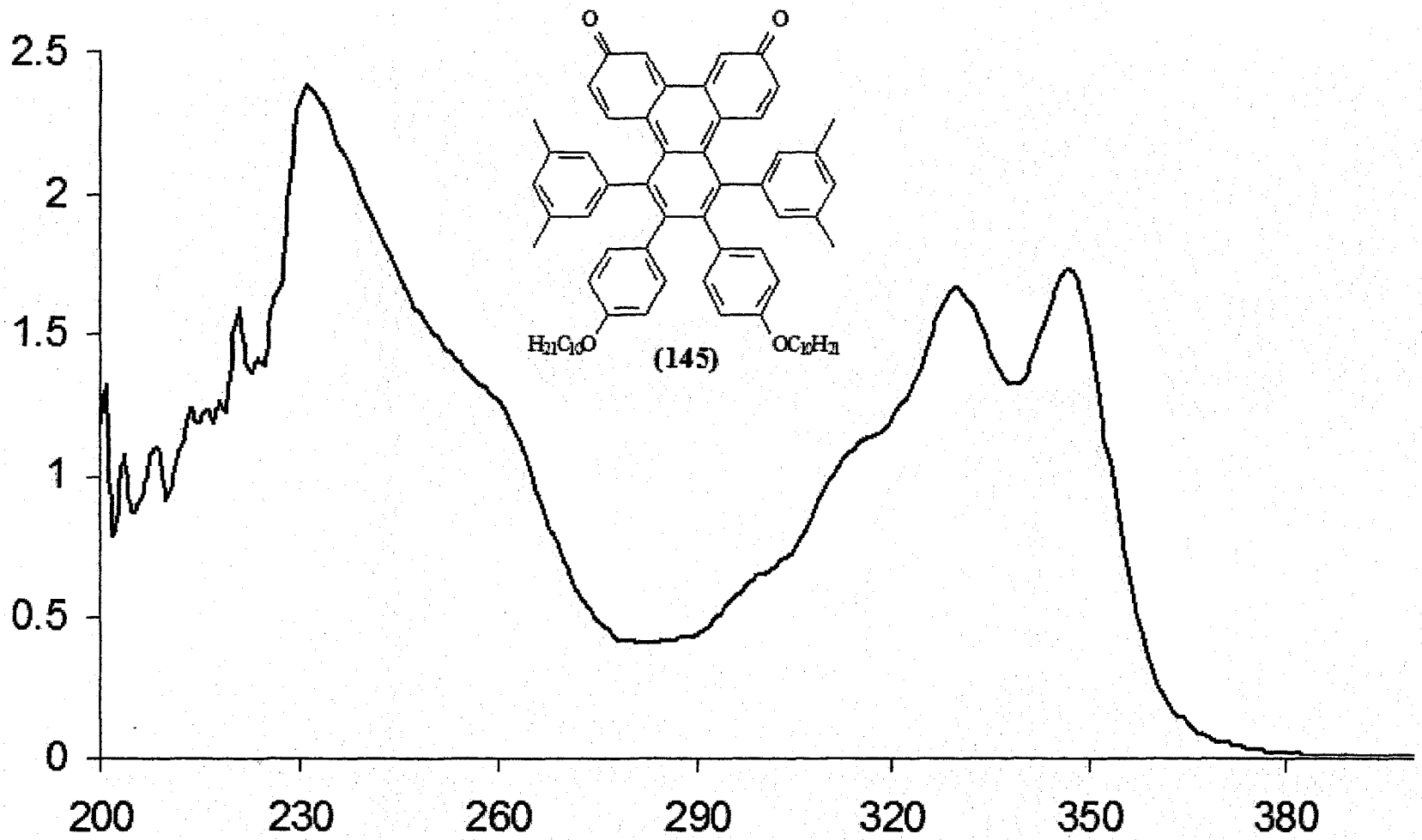
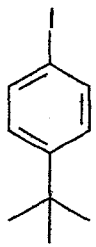
90
95
100
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
3654.21
3636.16
3621.37
3601.93
3744.61
3688.65
3675.73
3629.36
2924.26
2853.84
2358.71
2344.44
1734.28
1700.41
1684.45
1665.72
1654.48
1621.60
1602.80
1569.85
1539.59
1499.15
1456.80
1396.03
1375.56
1305.84
1294.36
1260.76
1245.90
1223.18
1171.44
1141.54
1118.25
1071.07
1061.55
986.36
936.46
898.71
861.60
852.54
829.55
768.07
752.40
723.19
700.44
674.28
669.00
665.10
653.39
$H_{21}C_{10}O$
(145)
$OC_{10}H_{21}$
O
O


2.5
2
1.5
1
0.5
0
200
230
260
290
320
350
380
O
O
$H_{21}C_{10}O$
$OC_{12}H_{21}$
(145)



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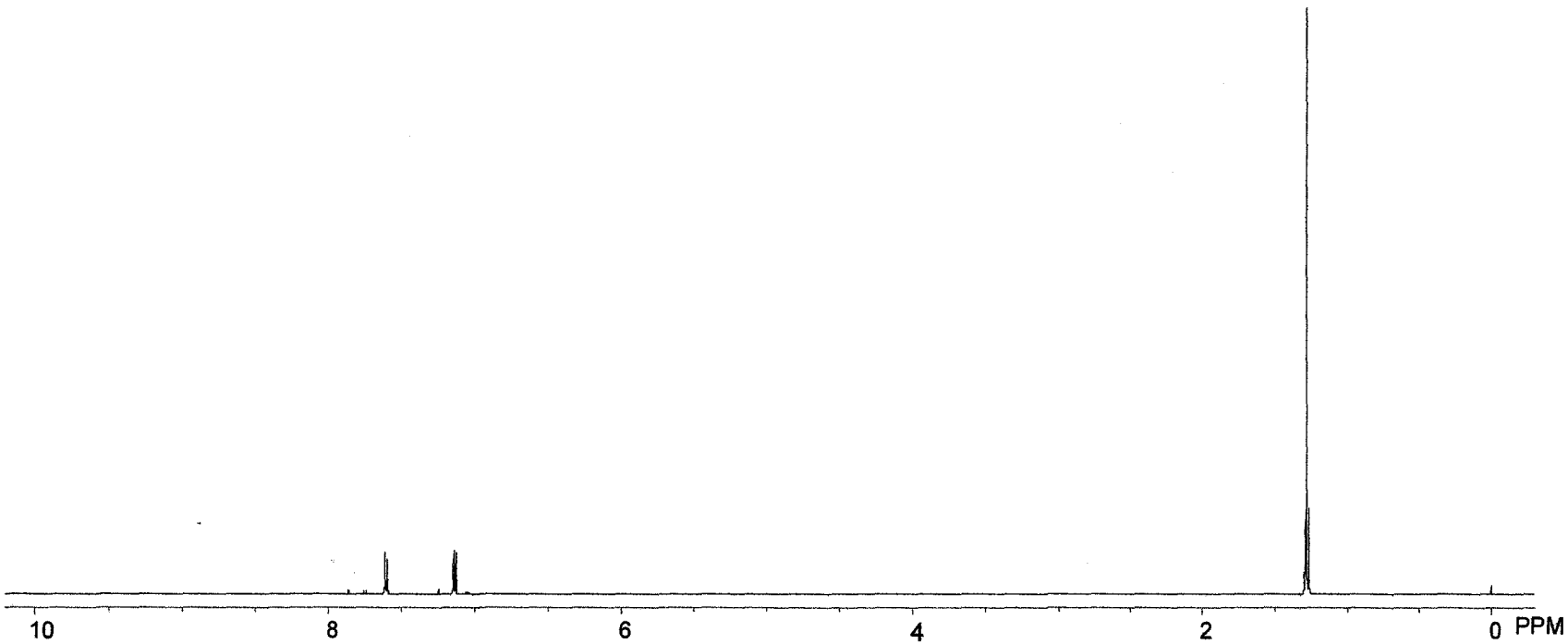

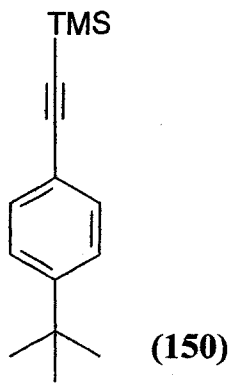

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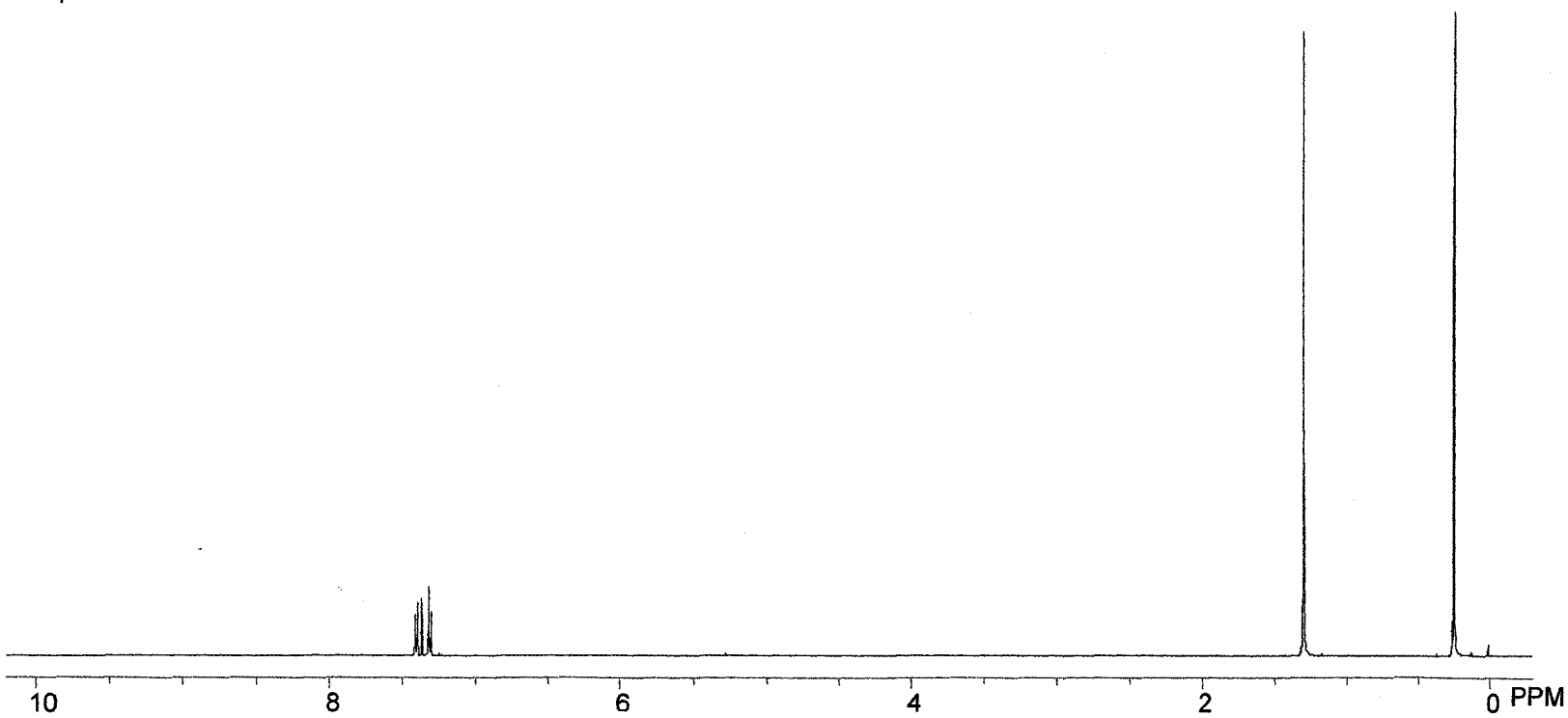

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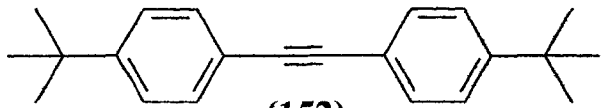
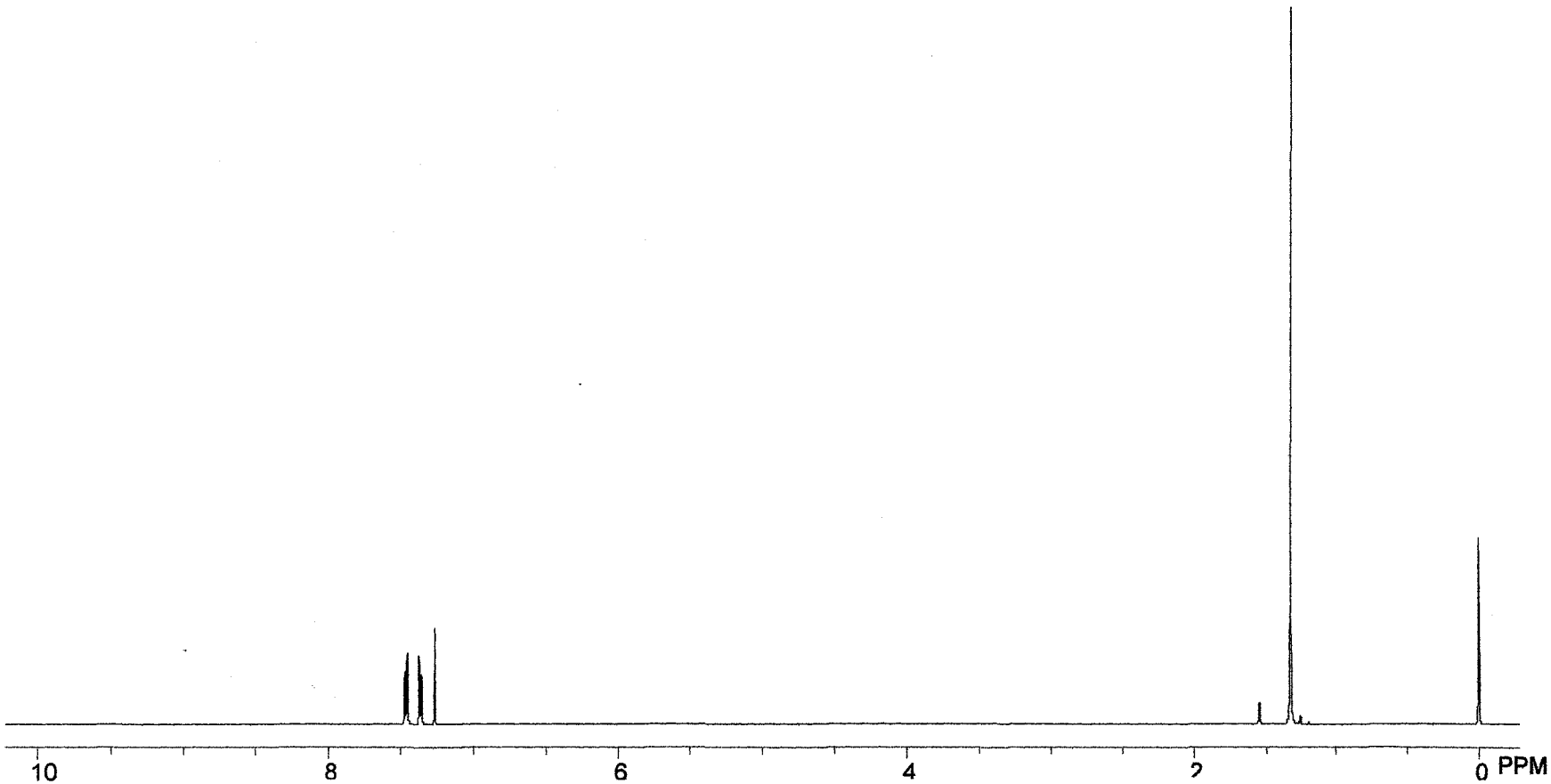


(152)



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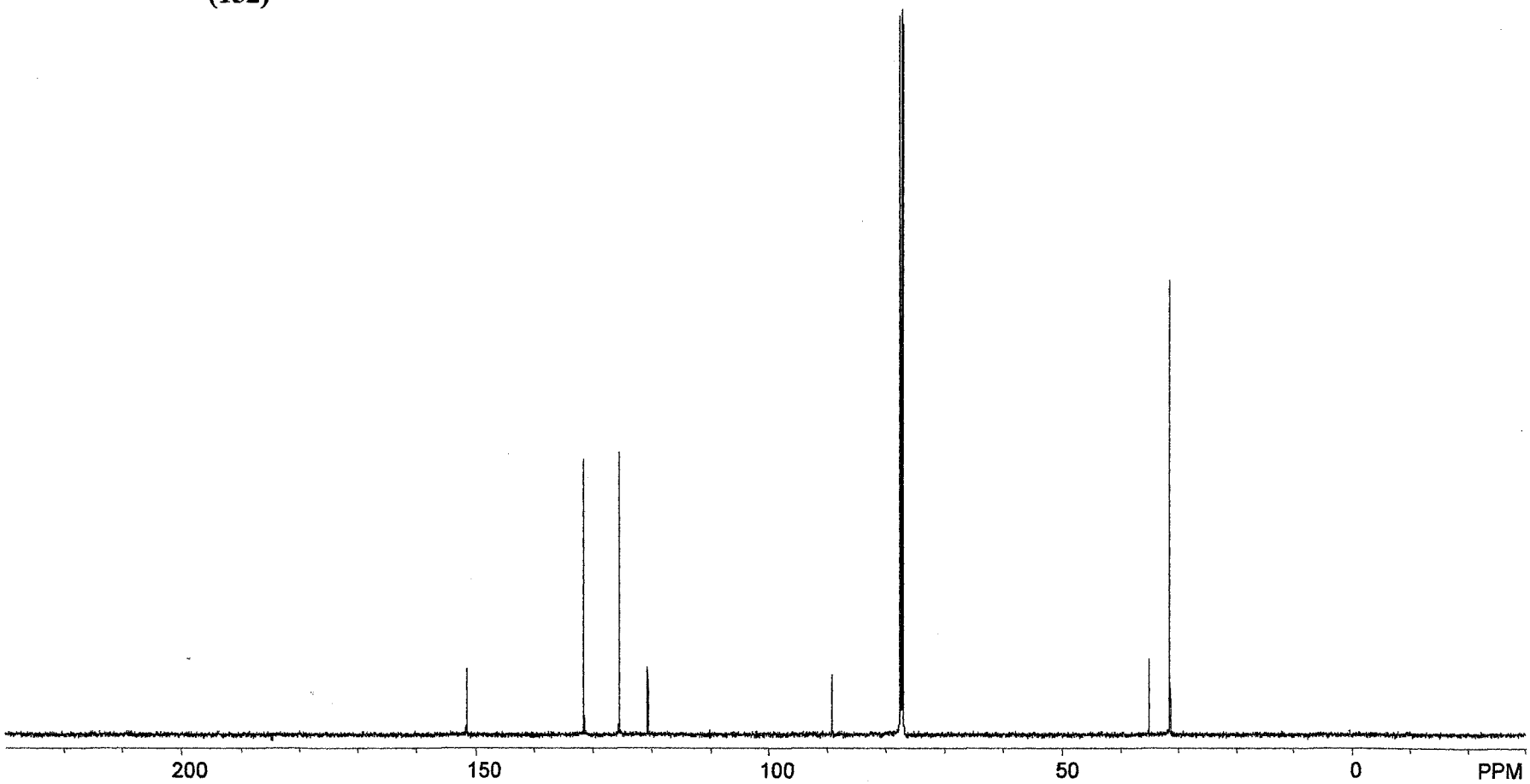

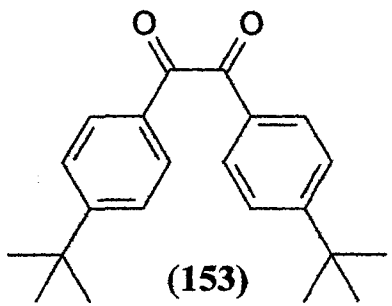

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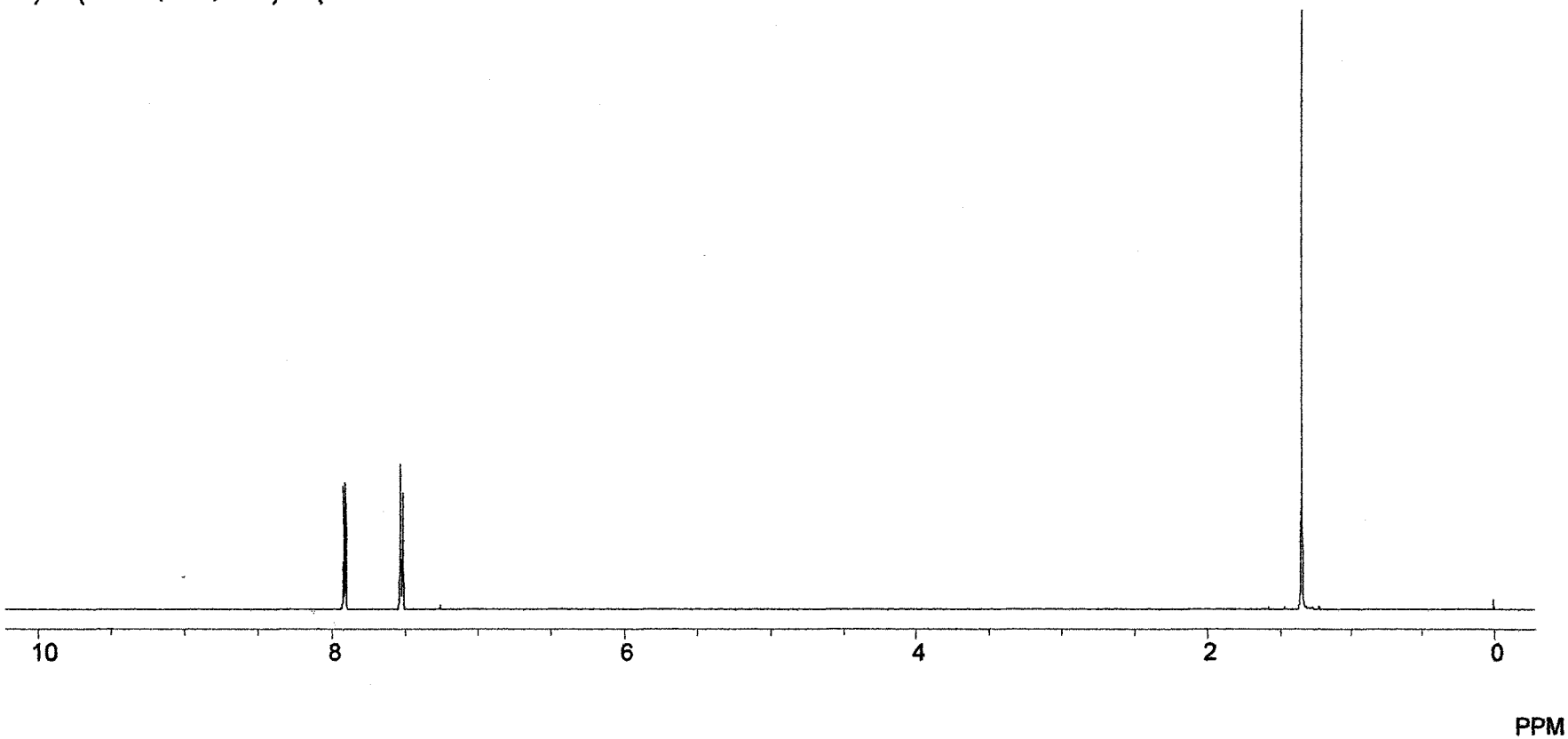

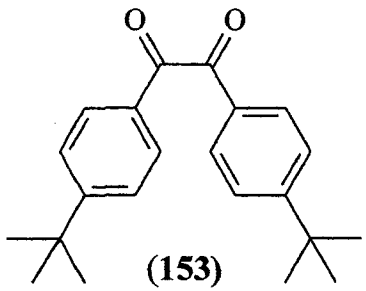

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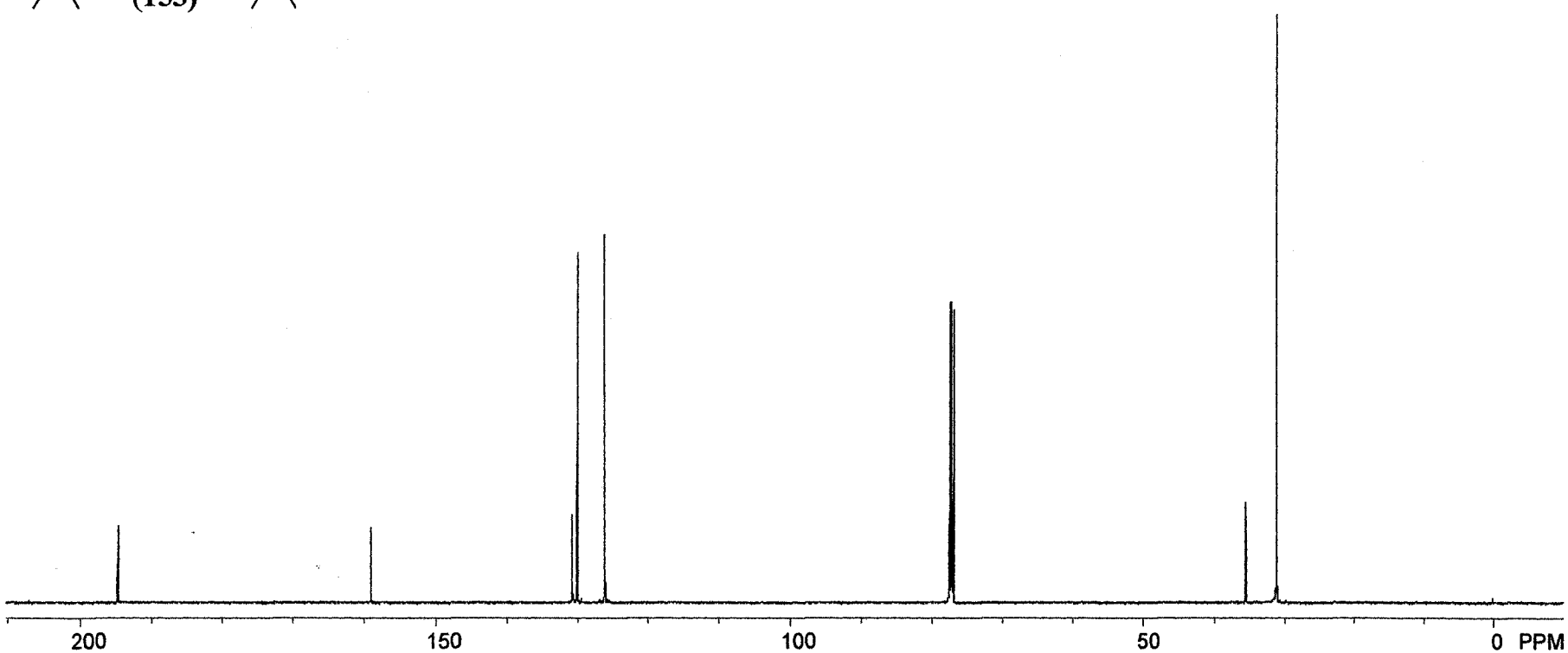

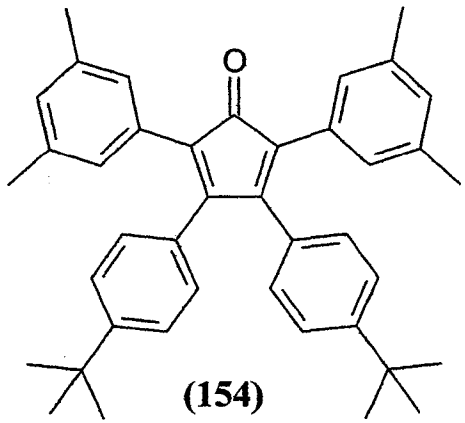

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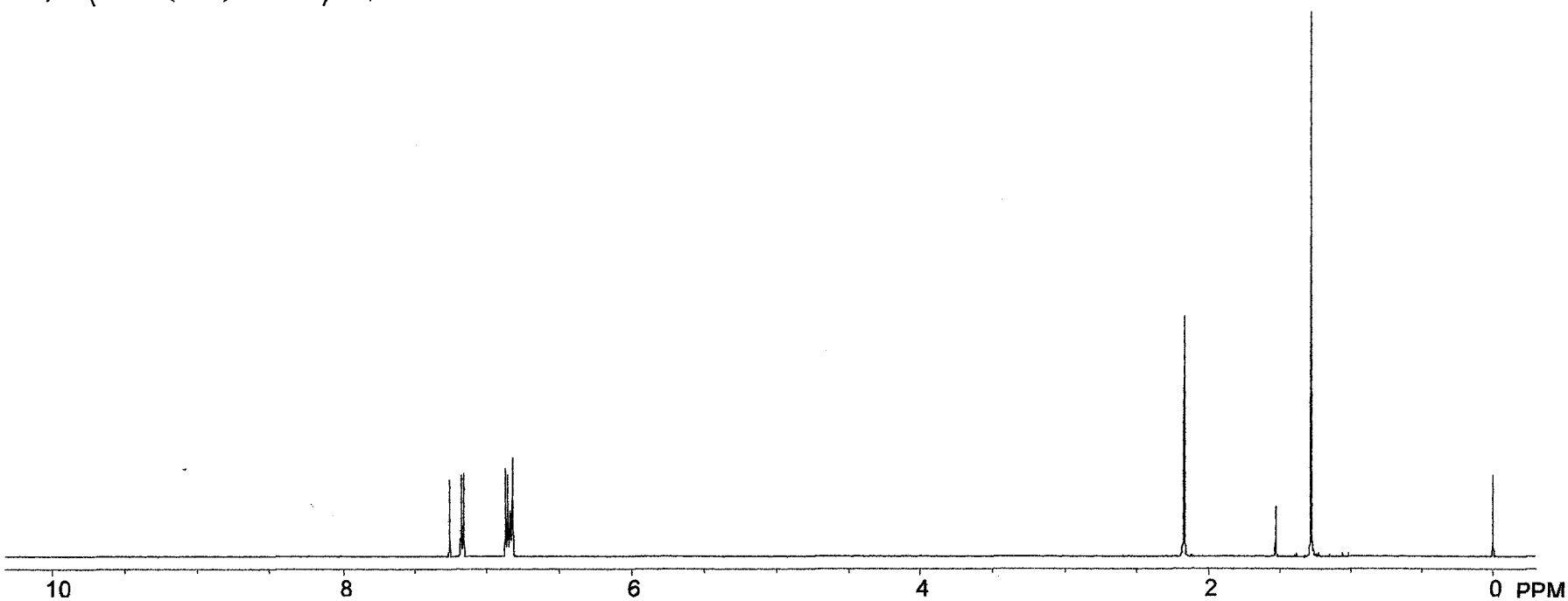

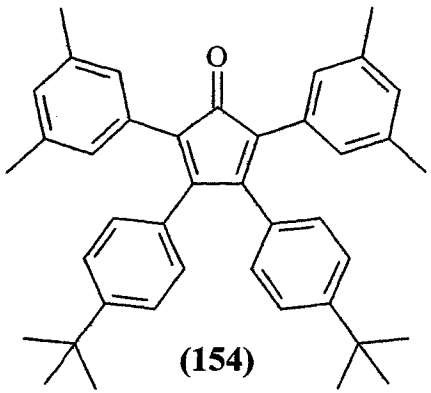

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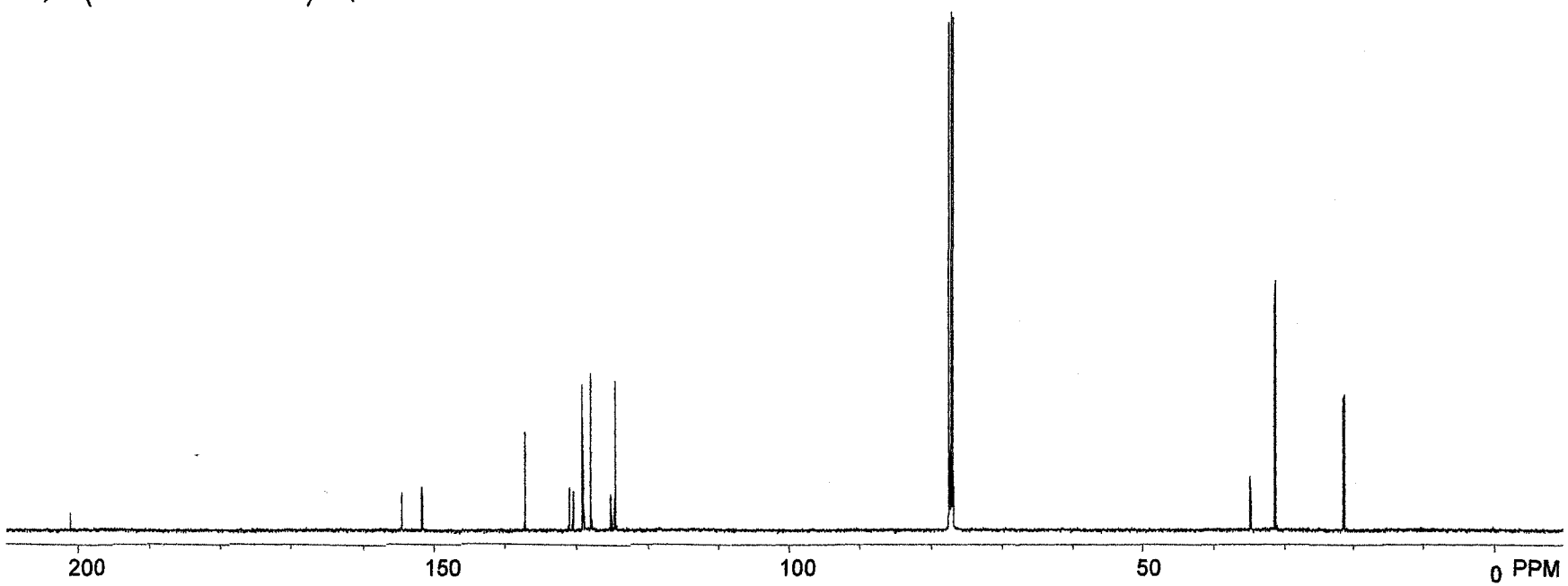

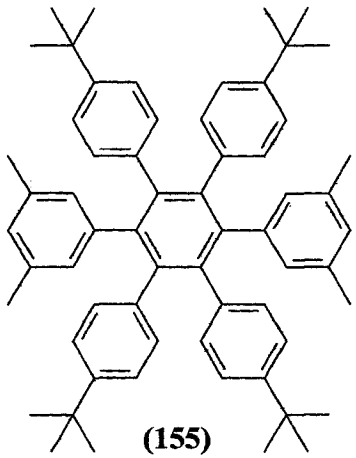

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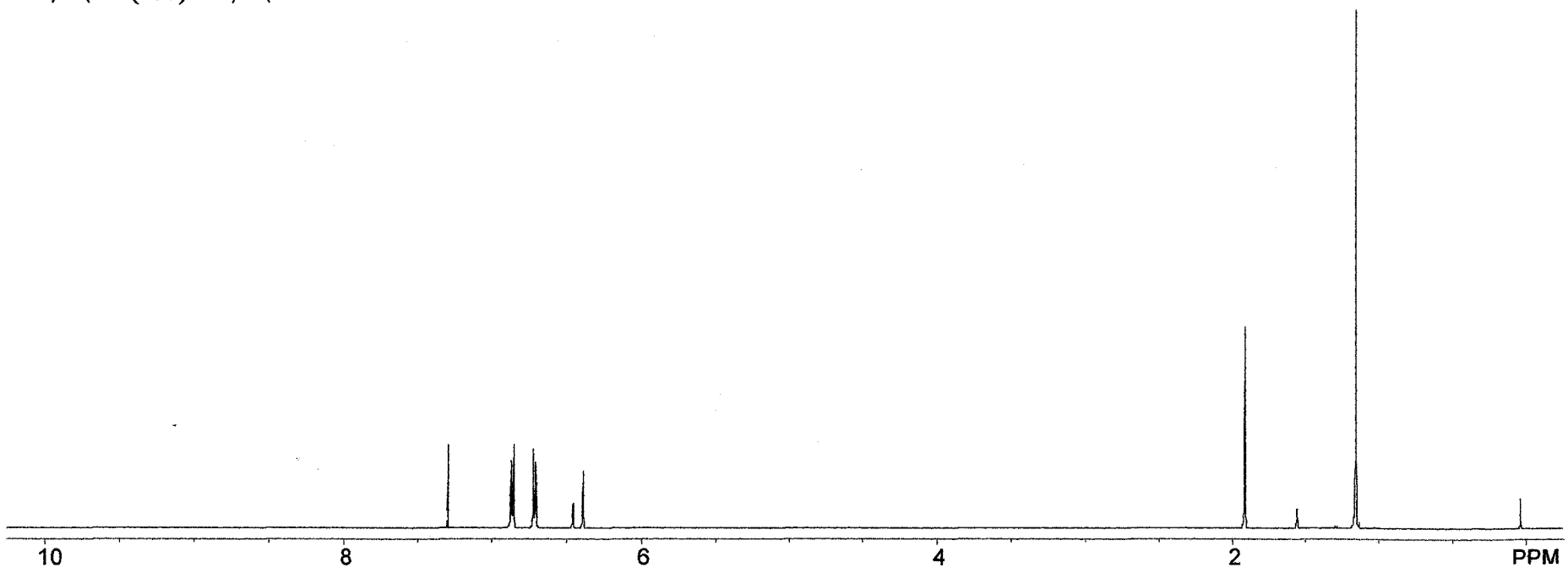

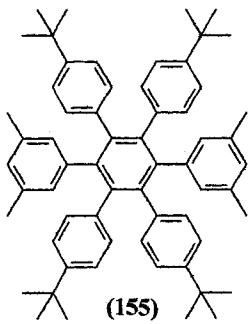

(155)